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**THERMAL EXPANSION OF REINFORCED
COMPOSITES - THERMAL HYSTERESIS EFFECTS**

G. L. DENMAN

TECHNICAL REPORT AFML-TR-65-279

MARCH 1966

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**AIR FORCE MATERIALS LABORATORY
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AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

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FOREWORD

This report was prepared by the Materials Engineering Branch, Materials Applications Division, of the Air Force Materials Laboratory, under Project No. 7381, "Materials Applications," Task No. 738106, "Design Information Development." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. Mr. G. L. Denman was the project engineer.

This report covers work accomplished from August 1963 to December 1964. The manuscript was released by the author in August 1965 for publication as an RTD technical report.

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This technical documentary report has been reviewed and is approved.

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ABSTRACT

The effects of thermal cycling and variable thermal history on the dimensional behavior of reinforced plastic composites are presented. Thermal expansion was used as the primary independent variable in studying the wide variations in composite dimensions with thermal treatment, collectively termed thermal hysteresis phenomenon. The composites studied were those currently considered in structural and ablative applications.

It has been found that the thermal expansion characteristics of a given composite may vary by more than 100 percent in cycling between room temperature and about 400°F. The most striking phenomena which is consistently observed is a decrease in the expansion coefficient to zero at about 200°F followed by an increase at higher temperatures. Studies completed in analyzing this behavior included the following: (1) internal stress behavior of the composite as reflected in tensile and flexural modulus characteristics, (2) second order transitions of the polymeric matrix, (3) moisture absorption in the matrix, and (4) thermogravimetric analysis of the matrix and composite. Correlations between analytical model predictions and experimental performance were made on the various composites studied. Extensions of these models in explaining and estimating the dimensional behavior of other composite materials are discussed.

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INTRODUCTION AND APPROACH

Reinforced plastic materials are being employed in ever increasing frequency for various types of applications, both structurally and as ablatives for thermal protection systems. Successful design with these materials is predicated on the availability of property data and knowledge of the thermal and mechanical stability of the materials at elevated temperatures.

In many applications, reinforced plastics are used as secondary structural members such as shrouds, fairings, and heat shields. To obtain successful joining to a primary structural, very accurate prediction of the dimensional behavior through knowledge of the thermal expansion characteristics is essential. Dimensional stability as a function of time, temperature, and environment are of first order importance in calculation of structural bond line stresses. Other considerations such as internal stress and thermal shock generate requirements for a complete understanding of the thermal expansion behavior of reinforced plastic materials.

Polymeric base composites for most aerospace applications are highly anisotropic which complicates the problem of accurately determining their properties. Typically a composite is fabricated from layers of woven fabric. The fabric is normally impregnated with 20 to 40 percent by weight of partially cured resin. Final molding and curing is accomplished under pressure at elevated temperatures. A composite formed in this manner is obviously anisotropic and since the polymeric matrix generally has a coefficient of expansion about 20 times greater than the inorganic reinforcements, variations in internal stress due to differential expansion become very important. Since these stresses exist primarily in the plane of reinforcement where the expansion is controlled by the reinforcement, it is important to define principle directions in this plane. These are the warp and fill directions which are parallel to the individual fibers. For plain or square weave fabrics these two directions are identical and the term "parallel to reinforcement" applies to either direction.

In the direction normal to reinforcement the resin is continuous or semi-continuous and therefore is predominate in determining the coefficient of expansion. Any effects of resin weight loss or shrinkage due to polymerization will strongly influence the expansion in this direction.

These and other complicating physical and chemical characteristics of polymeric base composites lead to large discrepancies in the thermal expansion data reported in the literature. Large cyclic variations in the coefficient of expansion have been reported; however, the important processes which contribute to this phenomenon have not been fully studied. This program was initiated to study these variations in a thorough and systematic manner. To do this laminates of variable composition were fabricated along with pure resin specimens. Complete material characterization with physical and mechanical property measurements was made. Thermal history was the primary independent variable although environmental effects were also considered.

Some of the variables found to influence the thermal expansion of a given material system include: percentage of each material in the composite, wetting characteristics of the resin, fabrication parameters such as cure time and temperature, debulking characteristics, residual internal stress state, moisture absorption, and thermal history. Some of these effects are discussed in References 1, 2, 3, and 4. The effects of thermal cycling (References 2 and 3) can be extremely important

in terms of designing with these materials since the complete thermal expansion characteristics are represented by a family of curves in terms of the various parameters mentioned above.

Thermal cycling usually produces a hysteresis effect in thermal expansion versus temperature. The hysteresis phenomenon appears as two basic types of cycles. In the first a gradual decrease in the slope of the expansion-temperature curve (coefficient of expansion) on heating to or slightly above the maximum post-cure temperature is observed. The cooling curve in this case has a higher slope more typical of a completely stable composite. The second type is manifested as a very sharp break or dip in the heating curve at elevated temperatures. In this region the coefficient of expansion decreases rapidly and in some cases may become negative. At higher temperatures the curve generally increases again to a typical value for the material. The cooling curve is usually smooth with a slope nearly the same as that obtained at the higher temperatures on heating, thus producing a hysteresis effect.

The first type of cycle described above is generally thought to be a result of removal of volatiles from the matrix. These volatiles may be the result of additional curing reaction or due to absorbed species such as water vapor. This effect is largest in the direction normal in the reinforcement where the resin expansion is predominate.

In the direction parallel to reinforcement there have been several plausible processes described to explain the sharp break in the curve and the hysteresis effect. Pears (Reference 3) has suggested that the effect is due to undercured resin since removal of volatiles and thus shrinkage of the resin occurs on heating. For materials post-cured at high temperatures the break or anomaly was considerably reduced. Possible effects of discontinuous reinforcement were also suggested, however, the results were not consistent enough to permit a more rigorous analysis.

Lazar (Reference 2) reported essentially the opposite findings. In subjecting phenolic-glass fiber materials to three different post-cure conditions, it was found that the expansion of the material with no post-cure was practically linear while the materials with post-cure temperatures of 325° and 450° showed a large anomaly in the expansion curves at 300°F.

Lazar attributes this phenomenon to residual internal stresses that exist in the laminate on cooling from post-cure temperature: There is said to be no mechanism for stress relieving on cooling for post-cured materials whereas the uncured resin would not retain this residual stress. The large contraction of the resin on cooling from initial post-cure temperature in relation to the glass fibers is the source of residual stresses. The observed anomaly is said to be a result of stress relieving due to loss of modulus or to softening of the matrix material at the second order phase transformation or glass transition temperature.

This program was initiated to investigate the above phenomenon through thermal expansion testing of standard resin-reinforcement systems under varying thermal and environmental conditions. As discussed above the thermal history of plastic laminates has a very pronounced effect on the thermal expansion characteristics. Therefore a systematic study of thermal expansion as a function of thermal cycling was accomplished. The maximum temperature the materials were subjected to in this thermal cycling was limited to the maximum post-cure temperature or slightly above to reduce the effects of gross resin degradation. Environmental effects were considered by first testing materials stored under very dry conditions at room temperature for

periods of time extending up to six months. Effects of room temperature stress relieving were studied in this manner.

Since removal of absorbed gases such as water vapor have been suggested to have important influences on the expansion characteristics the materials were also stored under conditions of varying humidity before running expansion curves. Thermogravimetric analysis was used to investigate material weight loss as a function of thermal history in order to establish the effects of removal of volatiles from dry samples.

Flexural strength and modulus were determined on samples conditioned under environments similar to the thermal expansion samples to study possible structural effects due to thermal cycling. Tensile properties were measured to provide information relevant to theoretical models developed to predict thermal expansion behavior of composites.

MATERIALS

The hysteresis effects discussed above have been found most significant for composites with phenolic resins although it has been observed for other matrix materials such as epoxy and phenyl silane resins. Continuous fabric type reinforcement was selected due to its wide applications and was considered to best illustrate effects of residual stresses. Therefore, a glass fabric-phenolic resin system was selected as the primary composite for investigation. The amount of mechanical and thermal property data available in the literature (References 5 and 6) was the basis for selection of the individual commercial materials. To investigate effects of varying resin and reinforcement systems, epoxy-glass fabric and phenolic-graphite fabric were also studied.

Hysteresis effects due to either additional resin curing and/or residual internal stresses are dependent on the total resin content of the composite. Therefore, the phenolic-glass fabric system was fabricated with three different resin percentages. Castings of the two resins (phenolic and epoxy) were obtained to provide information on the relative contribution of the individual composite constituents. The post-cure temperature cycles for all materials was two hours at 200°F, and one hour each at 250°C, 300°C, and 350°F. Table 1 gives a brief description of the materials and a summary of the measured physical properties and an index code to provide cross reference of each system. A complete description of each material with all fabrication parameters and physical property test data is given in Appendix A.

EXPERIMENTAL RESULTS

Thermal Expansion

The thermal expansion apparatus used in this investigation is shown in Figure 1. It consists of a quartz tube dilatometer with a linear variable differential transformer (LVDT) as the displacement sensing element. Horizontal operation is used in place of the more conventional vertical mode to control and minimize the compressive load on the specimen while maintaining precise alignment of the specimen. This factor is particularly important at high temperature when the elastic modulus of the laminates is very low.

The quartz tube is 7mm inside diameter with a solid quartz plug fused into one end, the specimen resting against the plug. A slot is cut near the plugged end to allow direct placement of thermocouples on the sample. A 6mm diameter quartz rod

TABLE 1
PHYSICAL TEST DATA SUMMARY

| MAT'L NO. | MATERIAL DESCRIPTION | WEIGHT % RESIN CONTENT | FLEXURAL STRENGTH | FLEXURAL MODULUS | BARCOL HARDNESS | DENSITY lb/ft ³ | VOID CONTENT % |
|-----------|--|------------------------|-------------------|------------------|-----------------|----------------------------|----------------|
| A-1 | Glass, Reinforced Phenolic Resin C.T.L. 91-LD | 23.5 | 73,000 | 3.8 | 72 | 121.5 | 4.4 |
| A-2 | Glass, Reinforced Phenolic Resin C.T.L. 91-LD | 28.5 | 68,500 | 3.8 | 86 | 122.3 | 0.124 |
| A-3 | Glass, Reinforced Phenolic Resin C.T.L. 91-LD | 35.5 | 66,000 | 3.5 | 70 | 115.6 | 0.391 |
| A-4 | Pure Cast C.T.L. 91-LD Phenolic Resin | -100- | 1,900 | 3.7 | 0 | 74.4 | 0.090 |
| A-6 | Graphite Fabric Reinforced Phenolic Resin C.T.L. 91-LD | 29.2 | 13,700 | 1.65 | 33 | 88.9 | 0.229 |
| A-7 | Glass, Reinforced Epoxy Resin - EPON 828 | 31.7 | 75,300 | 3.6 | 70 | 115.8 | 0.140 |
| A-8 | Pure Cast EPON 828 Epoxy | -100- | 13,450 | 0.49 | 40 | 77.0 | 0.083 |

is inserted into the tube as the push rod, with one end on the sample, the other resting against the displacement transducer. The quartz tube is clamped at the cold end with a brass collar. The LVDT and exciter-demodulator package provide a D-C millivolt signal to the Y axis of a Varian X-Y recorder. The signal from the LVDT is proportional to the position of the ferromagnetic core of the transformer which is of course equal to the expansion of the specimen minus the expansion of quartz.

Two specimen thermocouples are used, the output of one connected directly to the X-axis of the recorder, the output of the other to the heating rate control circuit. The thermocouples are imbedded in small holes drilled radially in the sample. The control signal is the sum of the thermocouple voltage and a continuously varying voltage obtained from a motor driven precision potentiometer. This signal is fed to a saturable core reactor temperature controller. With this system a controlled heating rate is obtained which can be varied from about $\frac{1}{2}^{\circ}\text{F}$ per minute to about 5°F per minute. In this work the normal heating rate was $1\text{--}\frac{1}{2}^{\circ}\text{F}$ per minute.

To study effects of temperature gradient, a sample was instrumented with several thermocouples, placed both internally and on the surface at several points along the length of the sample. Heating rates less than about 2°F per minute were found to result in less than 3°F maximum temperature differences in the sample. Effects of nonequilibrium due to polymerization and removal of volatiles were also studied by interrupting the heating process, then holding the sample at constant temperature. For most materials the effects were negligible except above maximum post-cure temperature. In this range the expansion would drop about 10 percent when holding at constant temperature for several hours. Larger effects were observed on samples stored under high humidity and on the pure phenolic resin samples during the initial heating cycle. Some of these effects are reported along with constant heating rate data. A complete description of the design, calibration, and operation of the dilatometer is given in Reference 7. As reported, the maximum probable error of the dilatometer is about $1\text{--}\frac{1}{2}$ percent for the temperature range used in this work.

The samples were stored in a desiccator to eliminate large amounts of absorbed water vapor. Several samples were tested in this "dry" condition over a period of time extending from several weeks to about six months after fabrication. Figures 2, 3, and 4 show the results parallel to reinforcement for the phenolic-glass materials, A-1, A-2, and A-3 respectively. Samples number 1, 2, and 3 indicate increasing storage time spanning the above time interval.

Sample number one for each material shows a significant anomaly between 200° to 300°F . In each case the slope of the curve decreases rapidly and for the A-1 material the slope is highly negative in this temperature range. Samples number 2 and 3 show very little hysteresis in this range which would indicate possible effects of aging at room temperature.

To investigate the effects of thermal cycling on dry phenolic-glass samples the thermal expansion of sample number one of each material was repeated several times. The results are shown in Figures 5, 6, and 7 with only the heating portion of the cycles plotted. As shown, the repeated runs are practically linear with run number 2 for the A-1 and A-3 materials showing a slight dip in the curve near 200°F . The trend for the curves to become smooth on repeated cycling as reported by other investigators was confirmed. The cooling curves for the repeated heatings are not shown since they were essentially the same as the heating curves, indicating very little hysteresis effects.

The sample length and weight were recorded before and after each thermal expansion test. In all cases the final measured net change in length was the same as recorded by the dilatometer, thus indicating that the transducer was accurately following the rather drastic changes in length.

The thermal expansion results normal to the plane of the reinforcement for materials A-1, A-2, and A-3 are shown in Figure 8. The initial heating indicates a significant hysteresis effect, increasing with increasing resin content as expected since, in this direction, the expansion of the resin is predominate. The expansion results for pure resin castings of the 91-LD phenolic (A-4) used in materials A-1, A-2, and A-3 are shown in Figure 9. The initial heating showed very severe effects with the final specimen length decreased by more than the total expansion obtained at 400°F on repeated heating. The results shown are an average of three samples with the maximum deviation between samples being small.

The thermal expansion of material A-6 (phenolic-graphite fabric) is shown in Figure 10 for both the normal and parallel directions. In the normal direction effects of resin contraction are clearly shown. The material appears to be very stable in the direction parallel to reinforcement.

Thermal expansion of material A-7 (epoxy-glass fabric) in the direction parallel to reinforcement is shown in Figure 11. In the parallel to fabric direction the curve breaks sharply at about 275°F. This material provided some very interesting results and will be covered in some detail in the discussion section below.

Thermal expansion of the pure epoxy casting (material A-8) is shown in Figure 12. A large and rather sharp change in slope occurred at about 300°F during the first cycle. Repeated cycles were smooth with only slight hysteresis effects.

In order to investigate the effects of moisture absorption on the phenolic glass materials, samples were stored at various humidity levels prior to thermal expansion tests. The humidity levels used were 0, 30, 60, and 90 percent. These were obtained by suspending the samples above solutions of glycerol and water in a closed container at room temperature. The percent by weight glycerol required for the various humidities was determined from Reference 8. The results of the thermal expansion tests at various humidities parallel to reinforcement are shown in Figures 13, 14, and 15 for material A-1, A-2, and A-3, respectively. The effect is demonstrated very clearly in Figure 12 for material A-1. Obviously a significant amount of water was removed from the specimen between room temperature and about 200°F when the samples had been conditioned at high humidity. The other two materials did not show the large dip; rather the slope or coefficient of expansion was decreased.

Mechanical Properties

The room temperature mechanical properties of each material were measured by the material fabricator and the results are given in Table 1. Each property value is the average of five specimens. All test methods were in accordance with Federal Specification L-P-406.

Several samples of each material were placed in the thermal expansion furnace and thermal cycled in the same manner as a normal thermal expansion heating. Subsequent room temperature flexural tests were obtained. The results indicated no significant effect since all values fell within the deviation of the average values given in Table 1. Sufficient samples were not available to perform a statistical analysis of possible effects.

Since the elastic modulus of the matrix is extremely important in analysis of the dimensional behavior of composites, tensile tests were performed on the two pure resin materials (A-4 and A-8) at elevated temperatures. The results are shown in Figure 16.

Thermogravimetric Analysis (TGA)

TGA tests were performed on two of the materials (A-2 and A-4) used in this investigation. Since the TGA results can be a very strong function of sample geometry, the data was obtained for rod type samples of approximately the same size as the thermal expansion samples. The apparatus used for these measurements is described in Reference 9. Heating rates were similar to those used in the thermal expansion tests. Results for the A-2 phenolic-glass and the A-4 phenolic casting are shown in Figure 17.

DISCUSSION

As previously mentioned there are two probable causes for the anomalies and hysteresis effects observed in Figures 2 through 8. One cause was additional polymerization or curing of the resin, resulting in loss of volatile components and shrinkage of the matrix. The other cause is based on internal stress variations as a result of the extreme differences in the coefficient of expansion of the resin and reinforcement.

Consideration of effects of additional resin curing can lead to partial explanation of the anomalies in the thermal expansion curves. Considering the first temperature cycle in Figure 9 (A-4 pure phenolic resin) we note a very large contraction or shrinkage near 250°F. If this shrinkage is typical of the resin in laminate form such as the A-1, A-2, or A-3 materials, the effect should be detected in all directions with the effect parallel to reinforcement reduced somewhat by the restraint of the glass fibers. However, the phenolic casting used in this program is considered to be considerably undercured as reflected in the hardness and strength values given in Table 1. The TGA results shown in Figure 17 also indicate a disproportionate loss in weight of the A-4 material compared to the A-2 laminate. The A-4 material was cured under high pressure and it has been suggested (Reference 10) that full curing does not occur under these conditions.

The thermal expansion results reported by Lazar for unpost-cured phenolic-glass composite are rather unusual. An essentially constant coefficient of expansion for the unpost-cured material from room temperature to about 470°F was reported. Although the exact material and initial cure cycles were not reported, unpost-cured or even moderately post-cured phenolic resin is not normally dimensionally stable. This fact is evident from the results on the A-4 material used in this program.

Expansion results in the normal direction for the three phenolic-glass materials should be more indicative of shrinkage of the resin system in the laminate. As shown in Figure 8 the observed shrinkage is slight with the exception of the A-3 material. This is as expected since the materials increase in resin content from A-1 to A-3. These results are not consistent with the observed anomaly in the parallel to reinforcement direction since the magnitude of the hysteresis is largest for the A-1 material. Therefore, it is difficult to attribute the total of the anomaly to effects of resin shrinkage due to additional curing.

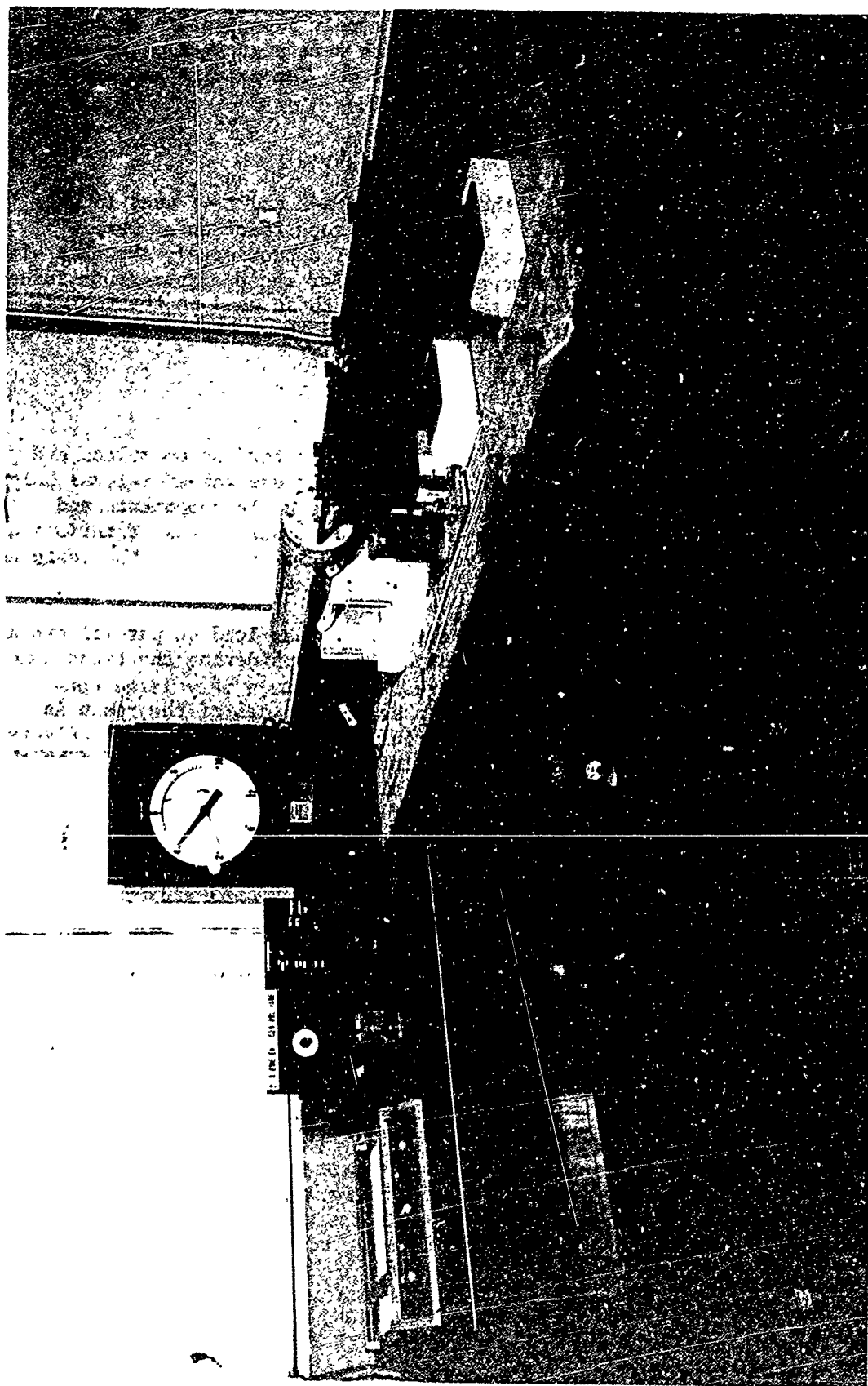


Figure 1. Quartz Tube Dilatometer for Thermal Expansion Measurements to 2000°F

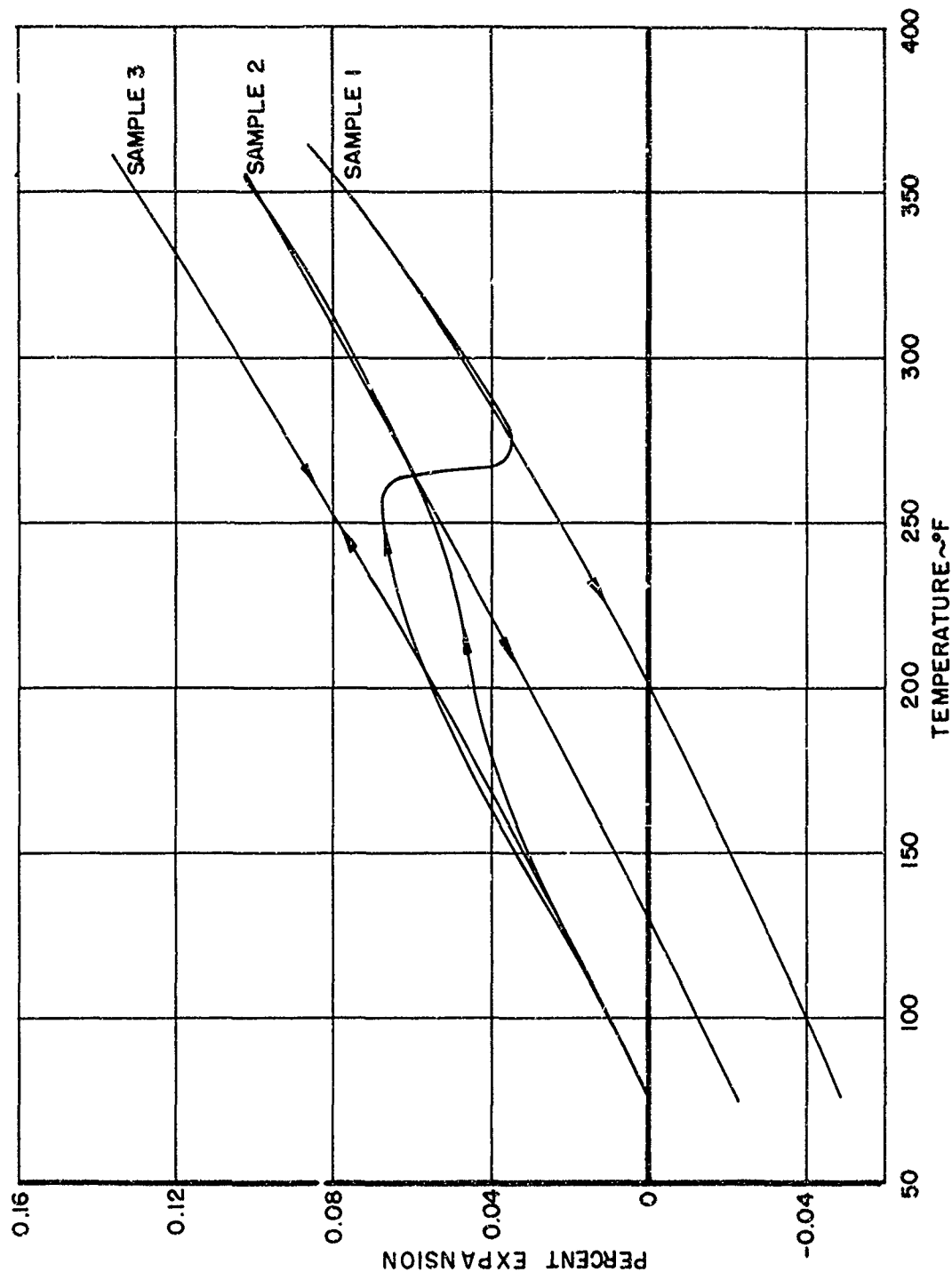


Figure 2. Thermal Expansion of Phenolic-Glass Fabric (A-1) Parallel to Reinforcement; First Cycle - Effects of Room Temperature Aging

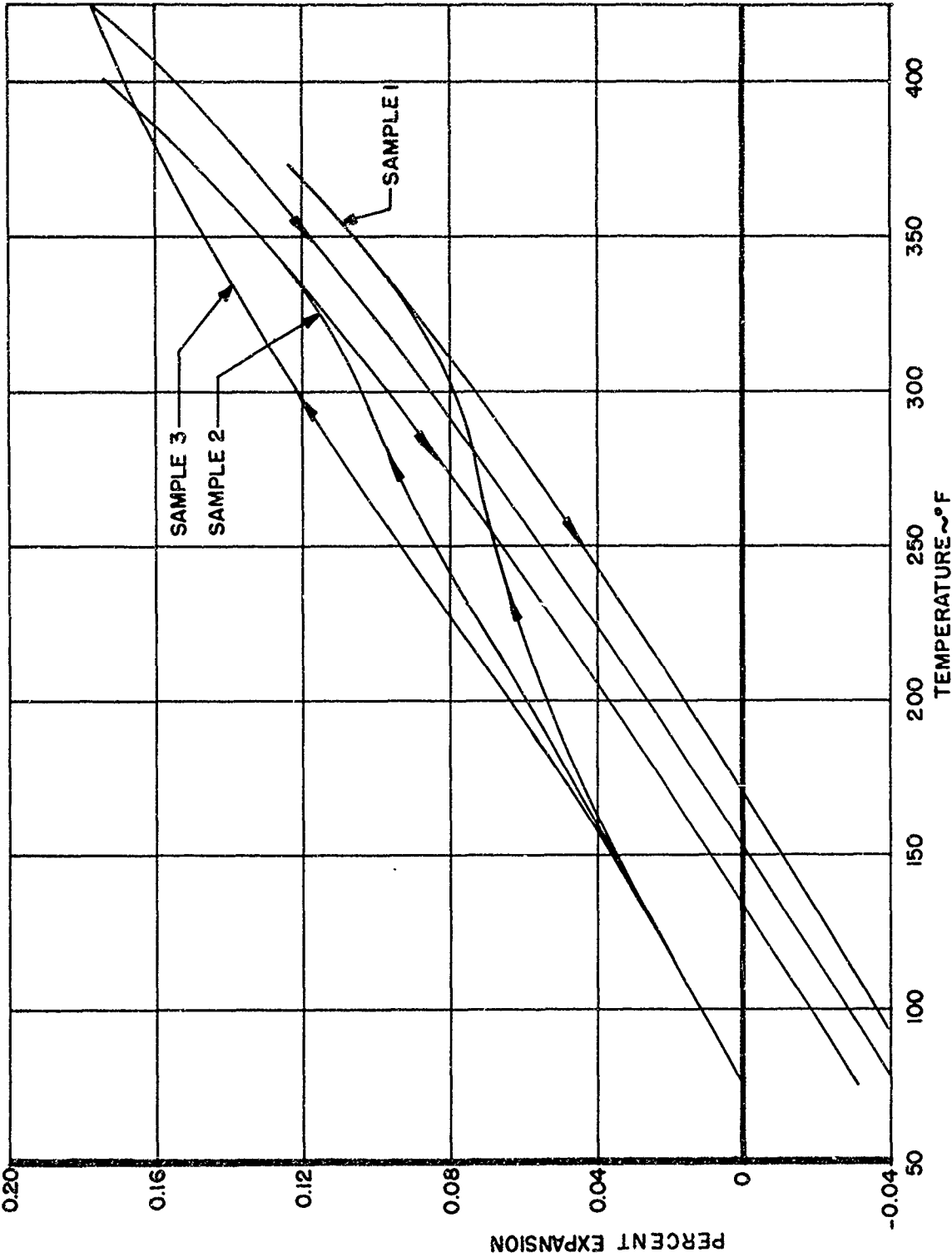


Figure 3. Thermal Expansion of Phenolic-Glass Fabric (A-2) Parallel to Reinforcement; First Cycle - Effects of Room Temperature Aging

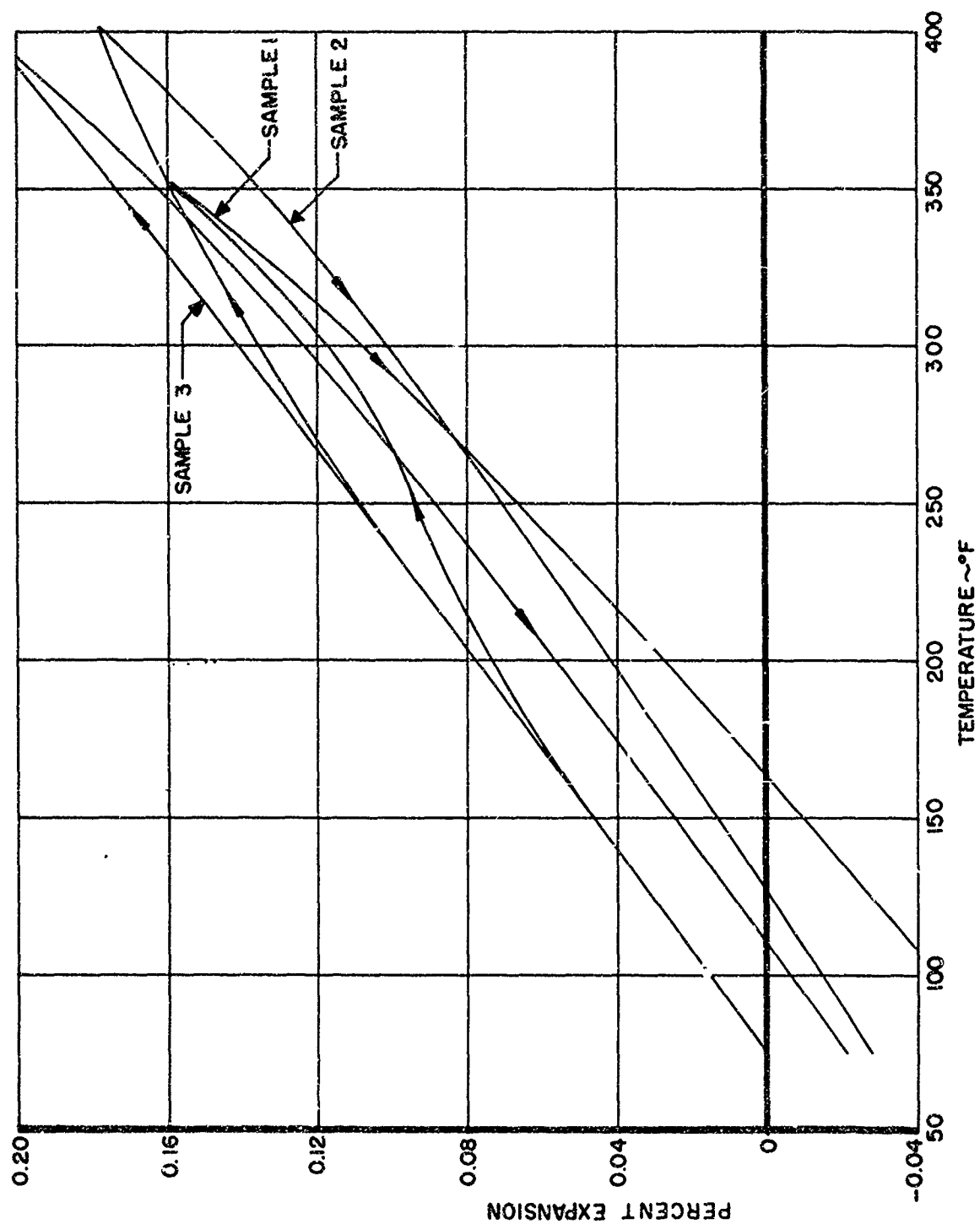


Figure 4. Thermal Expansion of Phenolic-Glass Fabric (A-3) Parallel to Reinforcement; First Cycle -- Effects of Room Temperature Aging

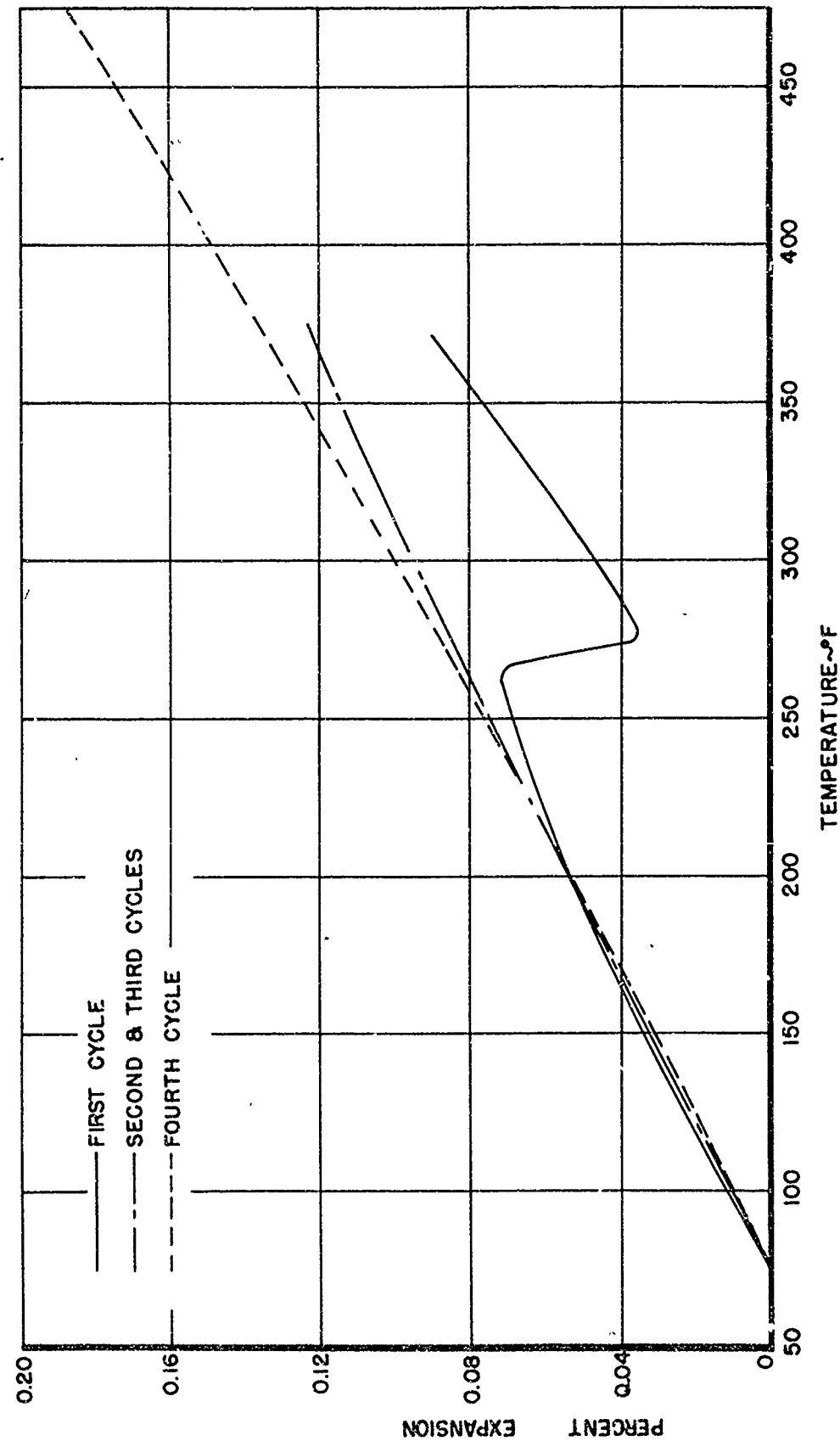


Figure 5. Thermal Expansion of Phenolic-Glass Fabric (A-1) Parallel to Reinforcement; Thermal Cycling

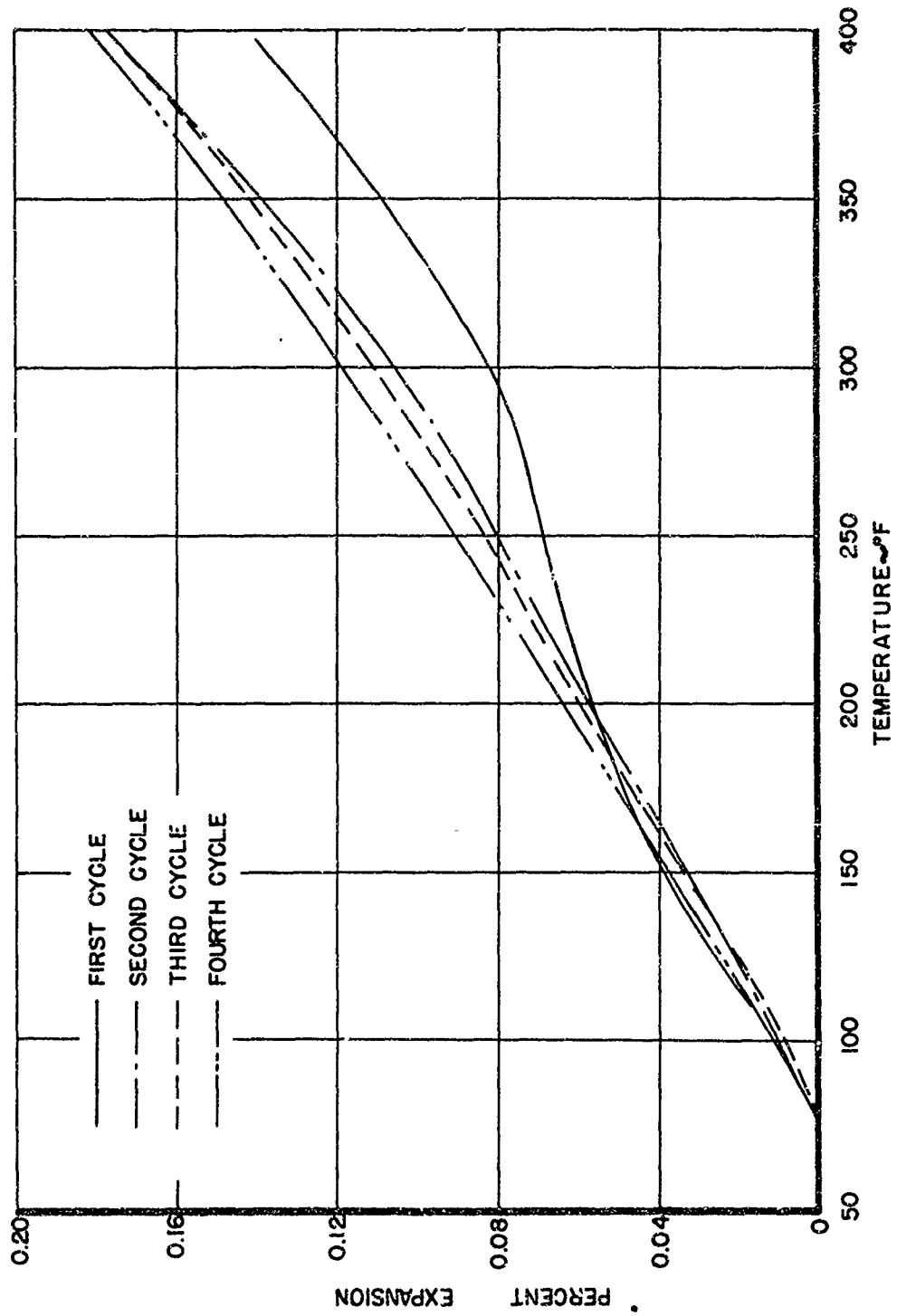


Figure 6. Thermal Expansion of Phenolic-Glass Fabric (A-2) Parallel to Reinforcement; Thermal Cycling

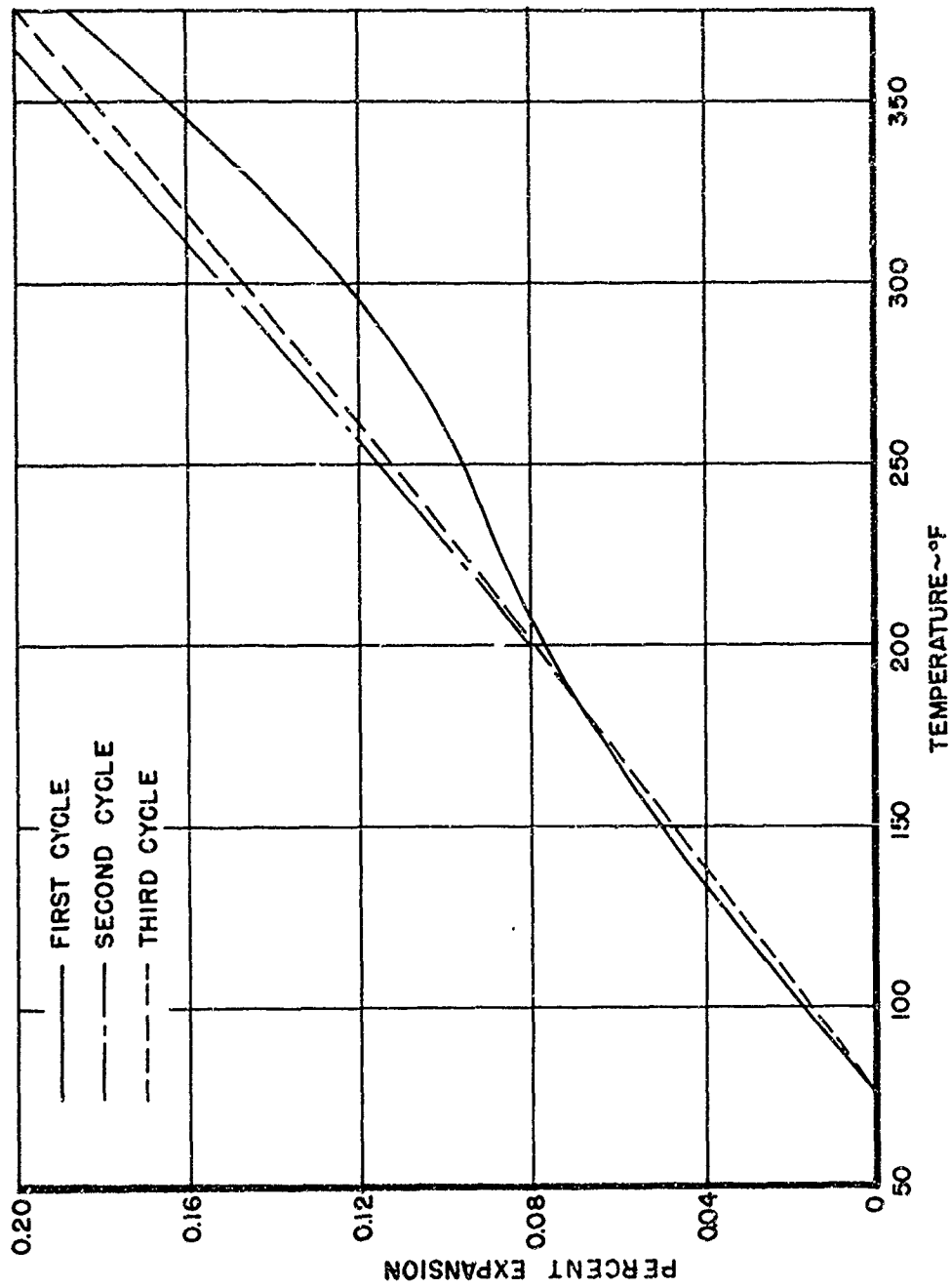


Figure 7. Thermal Expansion of Phenolic-Glass Fabric (A-3) Parallel to Reinforcement; Thermal Cycling

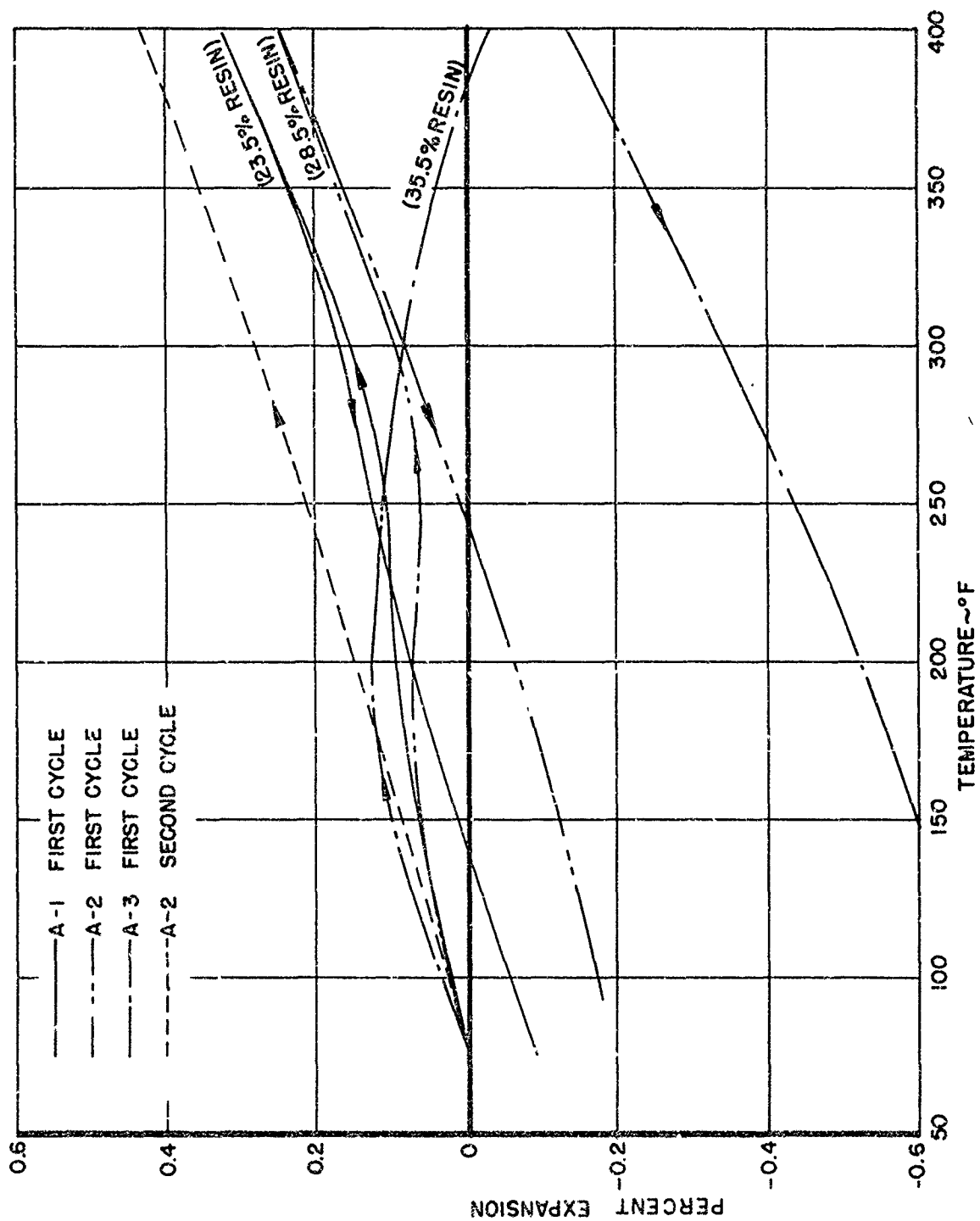


Figure 8. Thermal Expansion of Phenolic-Glass Fabric Normal to Reinforcement; Effects of Variable Composition

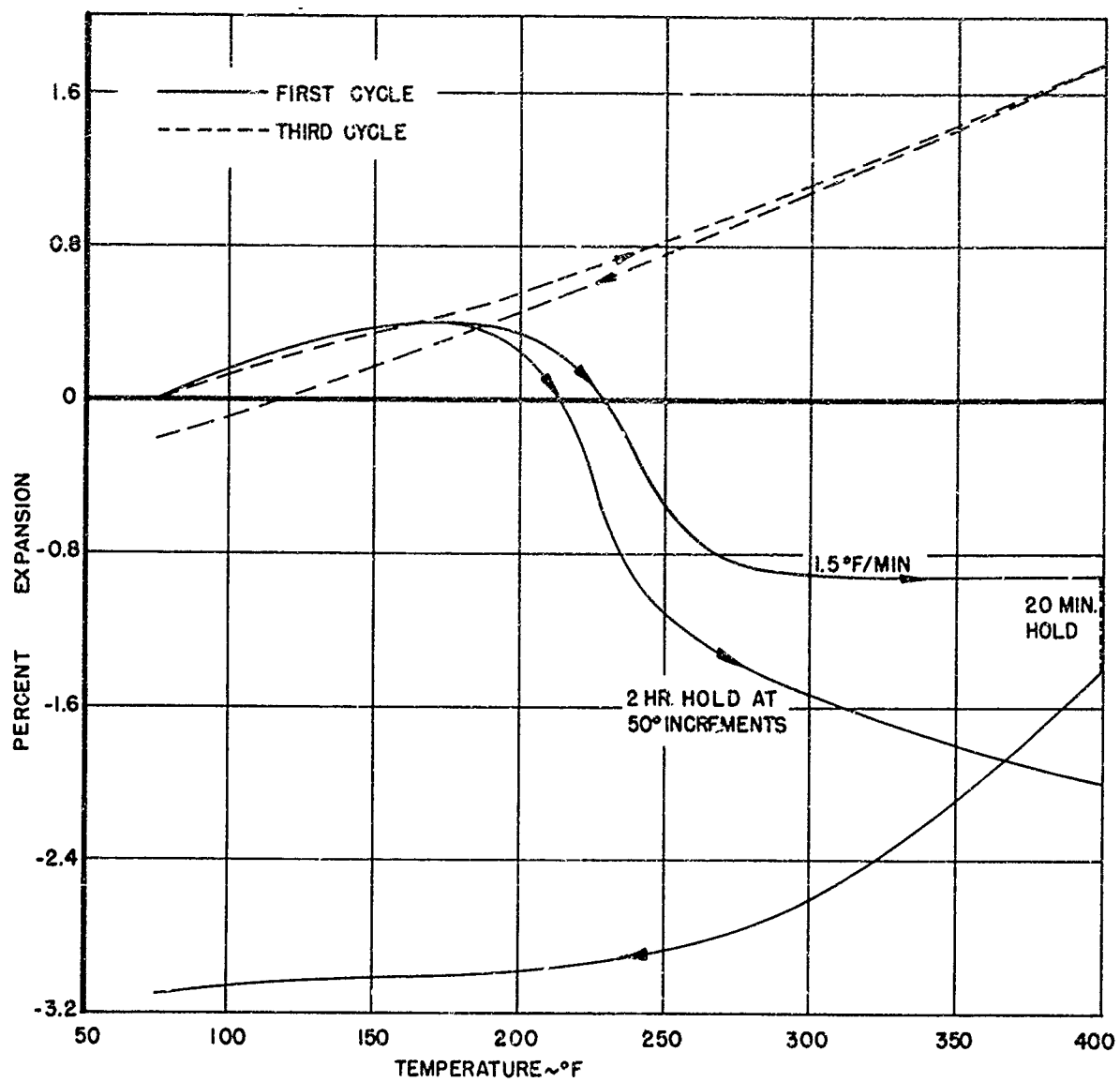


Figure 9. Thermal Expansion of 91-LD Phenolic Resin Casting (A-4)

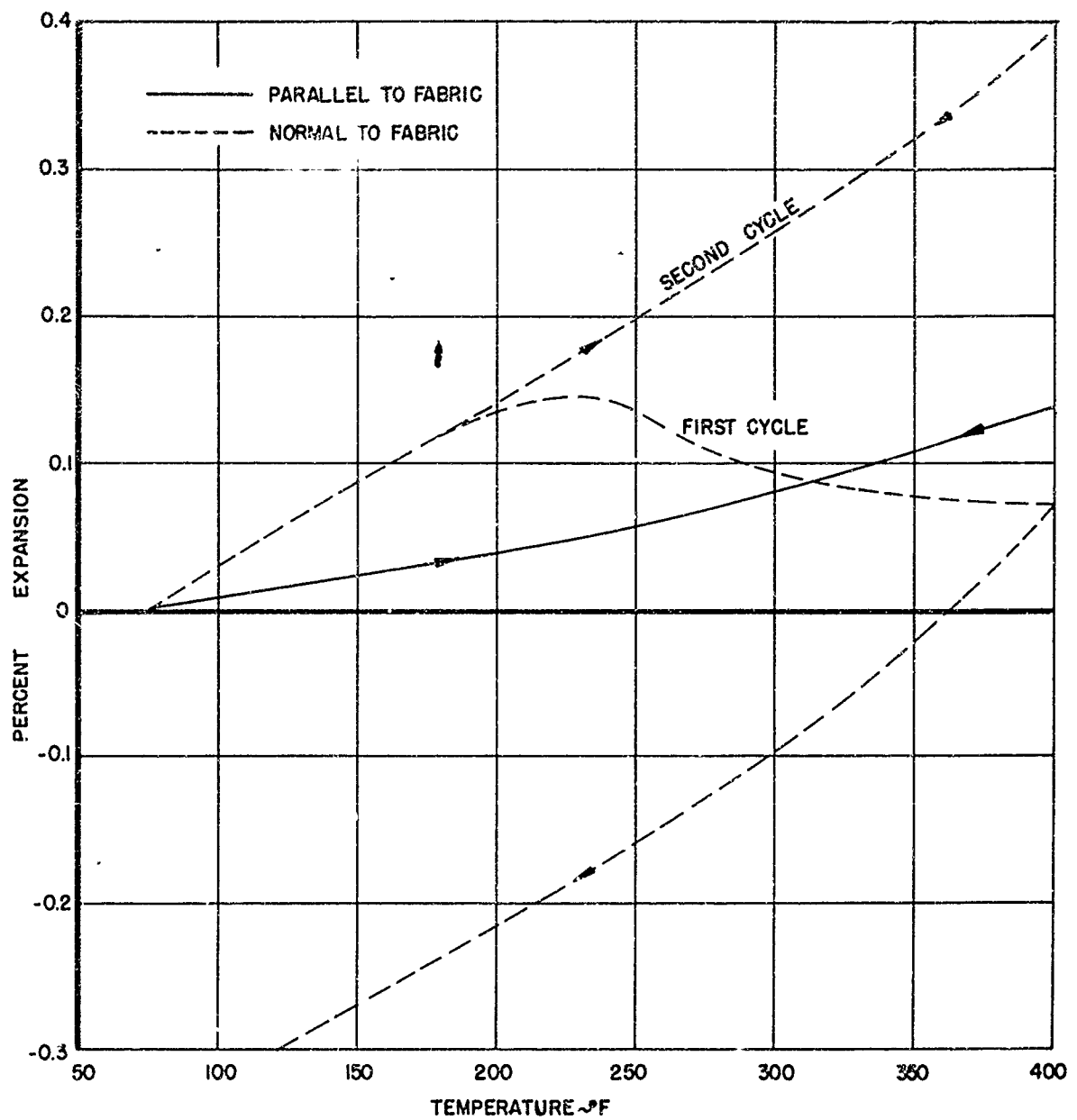


Figure 10. Thermal Expansion of Phenolic-Graphite Fabric (A-6)

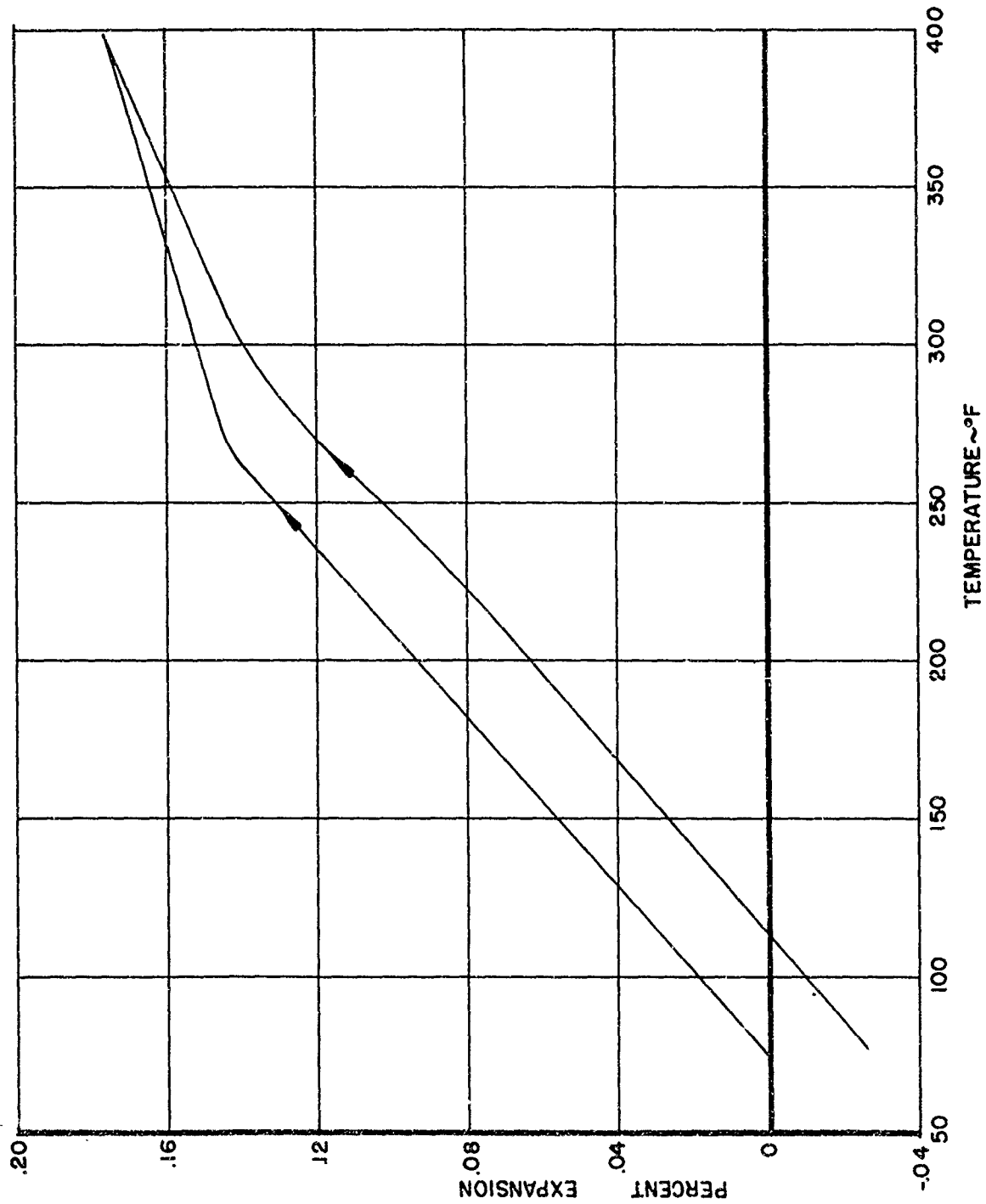


Figure 11. Thermal Expansion of Epoxy-Glass Fabric (A-7) Parallel to Reinforcement

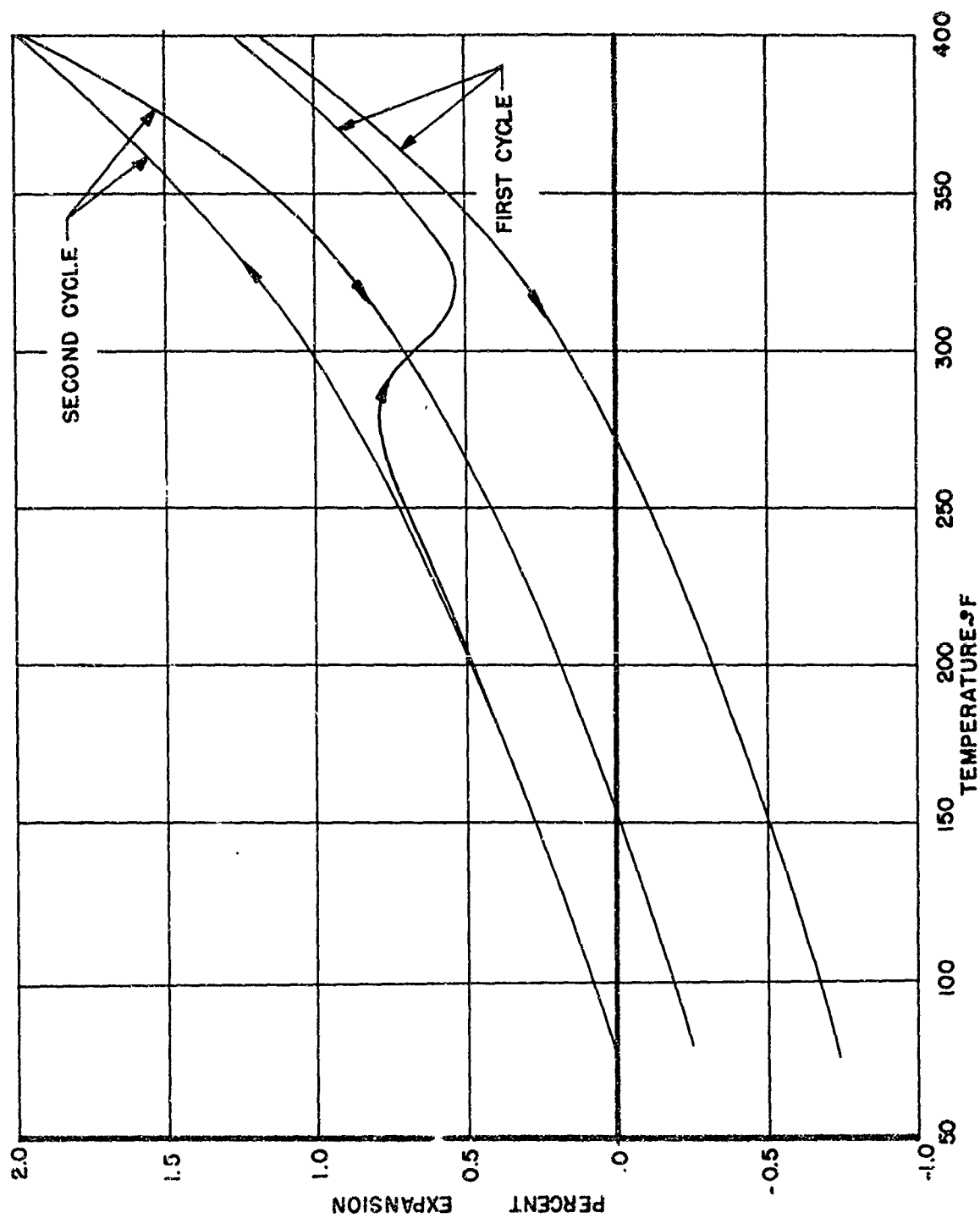


Figure 12. Thermal Expansion of Epon 828 Epoxy Resin (A-8)

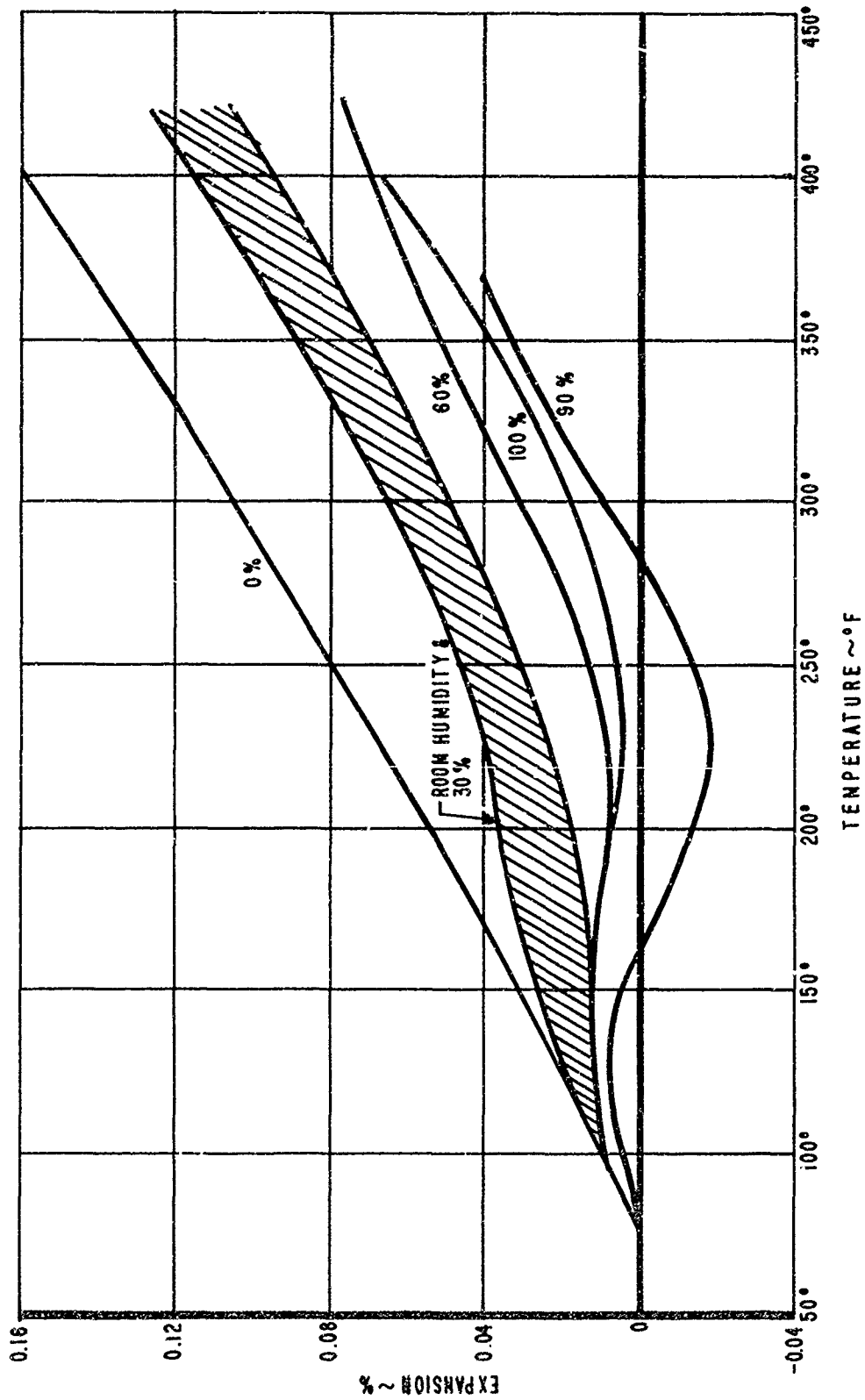


Figure 13. Thermal Expansion of Phenolic-Glass Fabric (A-1) Parallel to Reinforcement; Effects of Humidity

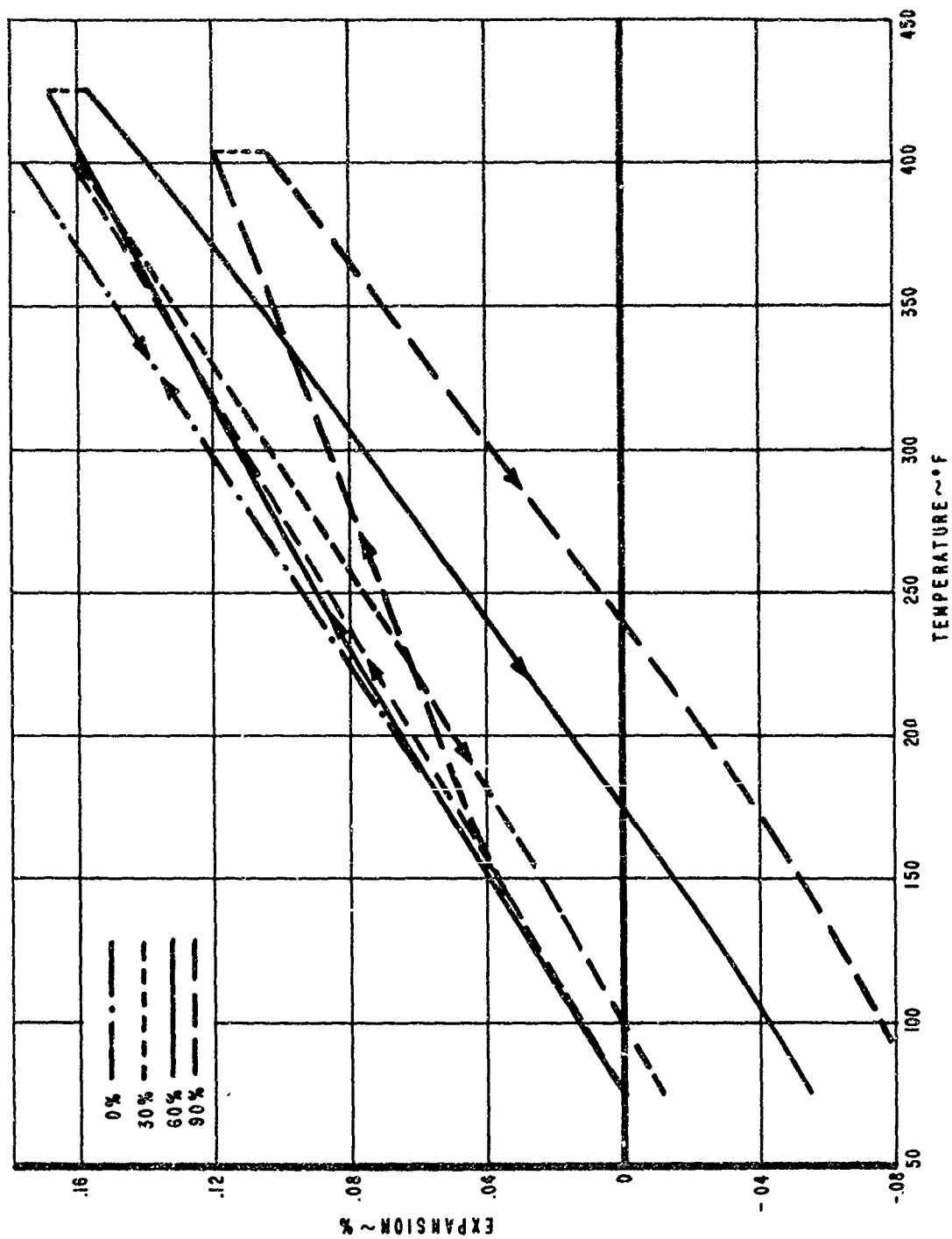


Figure 14. Thermal Expansion of Phenolic-Glass Fabric (A-2) Parallel to Reinforcement; Effects of Humidity

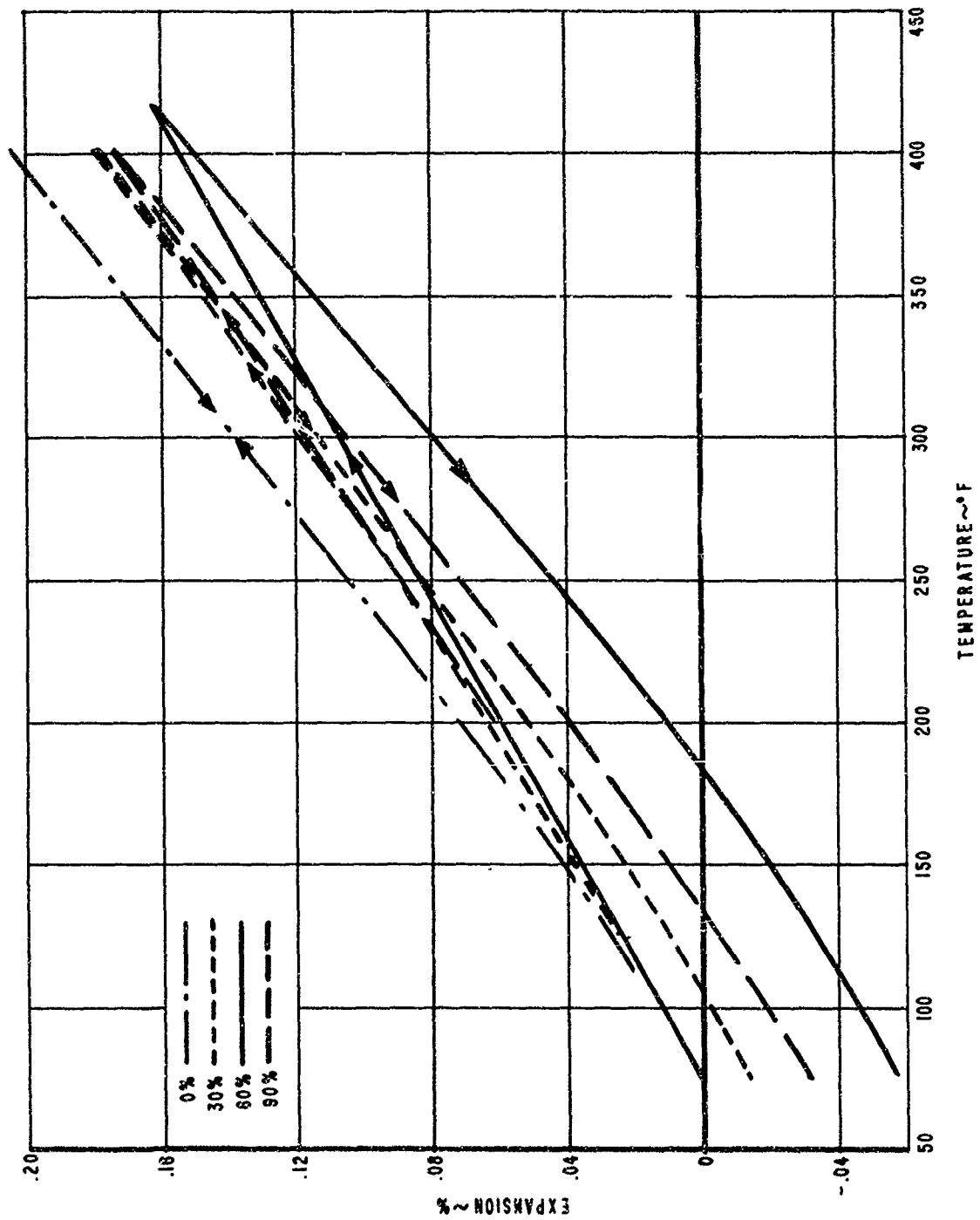


Figure 15. Thermal Expansion of Phenolic-Class Fabric (A-3) Parallel to Reinforcement; Effects of Humidity

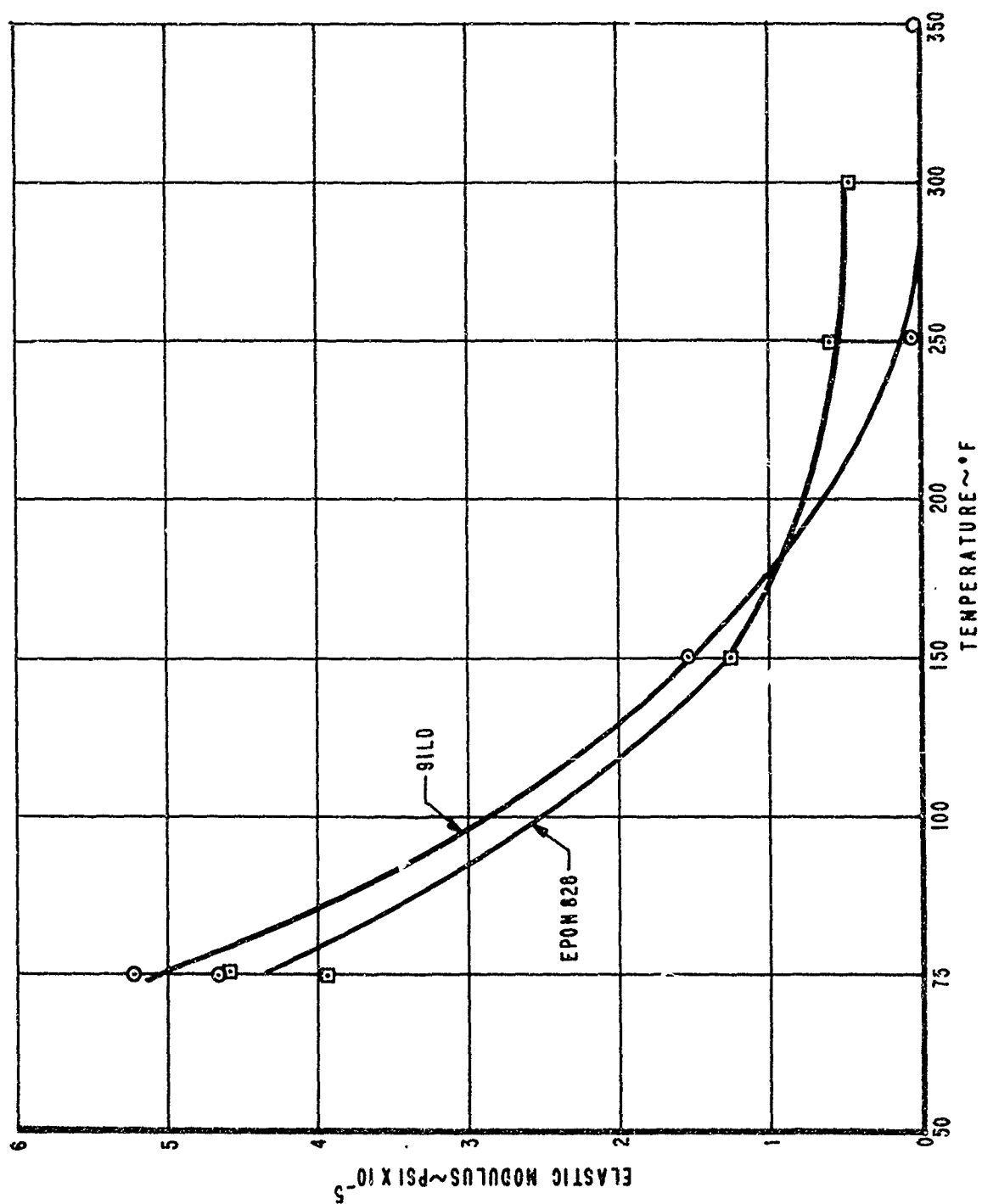


Figure 16. Elastic Modulus of 91-LD Phenolic Resin and Epon 828 Epoxy Resin

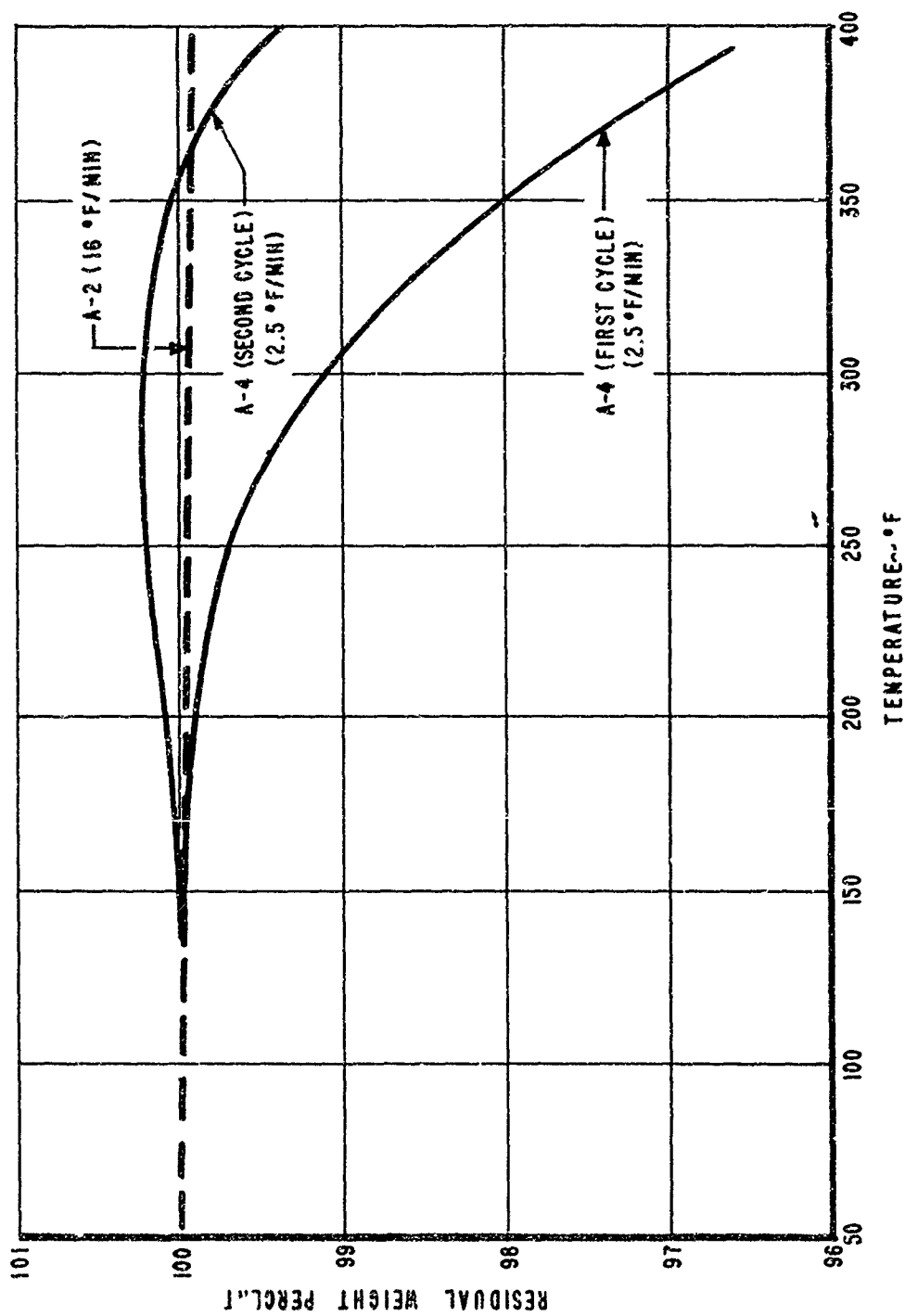


Figure 17. Thermogravimetric Analysis of Phenolic Resin (A-4) and Phenolic-Glass Fabric (A-2)

The internal stress considerations discussed by Lazar are based on resin softening at the second order transition temperature of the resin. However, if the resin modulus is reduced sufficiently to allow stress relieving as suggested, the expansion properties at higher temperatures would not be characteristic of a restrained fiber composite. Rather, the results should indicate the expansion of either unrestrained resin or glass fibers depending on the compression stress applied to the material under test. The higher temperature (above 300°F) expansion results on the phenolic-glass materials used in this program do not indicate an unrestrained system. The coefficient of expansion above 300°F is essentially the same as the initial value near room temperature.

To analyze possible effects of residual internal stresses as reflected in the parallel to reinforcement expansion anomaly, it is important to describe the stress state at room temperature. Since primary bonding of the resin and fibers probably takes place during fabrication at a temperature between 250° and 350°F for phenolic resins; on cooling, any differential dimensional changes between the resin and reinforcement will contribute to internal stress. Of course, the difference between the coefficient of expansion of resin and reinforcement will contribute to residual internal stress and for a phenolic-glass system this contribution will be large since the coefficients differ by a factor of about 20. Resin shrinkage due to curing after primary bonding will also contribute to residual stresses. The stresses of primary interest in this analysis are compression in the fibers and axial tension in the resin below curing temperature.

Malta and Outwater (Reference 11) have shown that residual stresses are not relieved on conditioning at room temperature, at least for the model used in their investigation. Here the model was one of radial tensile stress in the resin at the glass interface assuming the resin to be completely surrounded by glass fibers. Although this model has limitations, the fact that the stresses were not relieved is significant. The application of these results to other stress states in the resin are discussed by H. V. Boening in the same reference.

On composite heating, as during an initial thermal expansion test, the residual tensile stresses in the matrix will be reduced and finally relieved due to much larger expansion of the resin than of the reinforcement as discussed above. There must exist a temperature range at which, on the average, there is a zero axial stress between resin and fibers. This temperature may or may not be the temperature range at which primary bonding occurred. If the residual stresses are such that the proportional limit of the resin is not exceeded, then the "zero stress temperature" will be near the bonding temperature.

The magnitude of the residual stresses may be estimated by using an expression similar to the equation derived below in conjunction with prediction of thermal expansion of composites.

$$\sigma_M = \frac{(\alpha_M - \alpha_F) \Delta T}{\left[\frac{1}{E_M} - \frac{v_M}{v_F} \frac{1}{E_F} \right]}$$

where,

σ_M = tensile stress, psi

α = coefficient of expansion, in./in./°F

v = volume fraction

E = elastic modulus, psi

ΔT = change in temperature, $^{\circ}F$

M, F = subscripts for matrix and reinforcement, respectively

Using typical values for the physical properties of phenolic and glass fibers given in Table 2 in a system of 50 percent by volume reinforcement ($v_F = 0.25$ since only half of fibers are active in either warp or fill directions), the residual tensile stress in the resin at room temperature would be about 1200 psi. From tensile strength measurements, the yield strength of the A-4 phenolic resin is estimated to be above 1200 psi. Although the yield strength and residual stresses should be computed at intermediate temperatures, it is doubtful that any yielding will occur. Lack of proper strength data prevents a rigorous study of this effect.

The zero stress temperature will probably be between 250° and $350^{\circ}F$. As the material is heated through this temperature range on the first cycle after post-curing, the dimensional behavior of the laminate may be strongly affected by an inversion of stresses. That is, below this temperature the fibers are in compression and above the fibers will be in tension. The effect would occur over a fairly large temperature range since obviously the bonding of each fiber is not identical.

The observed anomaly for dry samples is probably a combination of redistribution of stresses as described above and resin shrinkage due to further curing. This is opposed to effects of stress relieving due to resin softening at the glass transition temperature.

Figures 2, 3, and 4 provide evidence that prolonged storage at room temperature will result in stress relieving. For each of the phenolic-glass materials the anomaly discussed above was strongly evident for the samples run within a few weeks after fabrication. On storage for several months the anomaly was not observed to any significant extent. The results normal to fabric reinforcement were not affected, thus eliminating possible effects of significant loss of trapped volatiles in the materials.

Figures 5, 6, and 7 indicate that stress relieving occurs on heating to or above the maximum cure temperature. In each case the repeated thermal expansion tests on the same sample resulted in smooth and unbroken curves.

The results for the A-7 material (epoxy-fiberglass) parallel to reinforcement shown in Figure 11 is considered to be an example of a system where resin softening results in expansion of an unrestrained two phase system. At $275^{\circ}F$ the curve bends over sharply and above this temperature the expansion is essentially equal to the expansion of the "E" glass reinforcement. It is felt that the compressive load on the specimens in the dilatometer is sufficient to deform the resin at this temperature. Very little hysteresis is observed as the cooling curve follows the general shape of the heating curve. These results were duplicated for several samples and were unchanged with repeated cycling with a given sample.

Humidity Effects

The effects of conditioning the three phenolic-glass materials (A-1, A-2, and A-3) at various humidity levels are clearly demonstrated in Figures 13, 14, and 15. In general all samples used in these tests had at least one prior temperature cycle in the expansion apparatus. Therefore, possible effects from residual stresses and resin cure should not be involved. The weight and length of each sample was recorded before and after thermal expansion tests. The dry weight and length after each test was essentially the same, thus indicating that materials were stable in this temperature range on repeated cycling.

As shown in Figure 12, material A-1 is very strongly affected by conditioning at high humidities compared to the other two phenolic-glass materials. This is attributed to the rather high void content of the A-1 material which is typical of laminates with less than 25 percent resin content. Void content of each material is given in Table 1.

Thermal expansion of samples containing large amounts of moisture is dependent on heating rate. This was not investigated to large extent, but in general, low heating rates shift the minimum in the curve to lower temperatures while high heating rates shift it to higher temperatures. The greatest significance of the effects of humidity conditioning is the change in the average coefficient of expansion over the temperature range of 75° to 400°F. For the A-1 material the dry sample has an average coefficient of about 5.1×10^{-6} in./in./°F, whereas the samples conditioned at high humidity have an average value of about 1.8×10^{-6} in./in./°F.

Expansion Phenomenon in Fiber-Reinforced Composites

For fiber-reinforced composites the most reasonable model to use in studying the thermal expansion in the direction parallel to fibers is one of stress equilibrium between matrix and reinforcement in composite systems. If good wetting and bonding exists between matrix and fibers, this model should adequately describe the stresses produced from differential expansion between matrix and reinforcement. An element of matrix and fiber is shown in Figure 18, with Figure 18a showing the system in initial stress equilibrium at a given temperature.

Figure 18b shows the system for a change in temperature ΔT , with unrestrained expansion of matrix and fiber. Figure 18c indicates the final stress of equilibrium position, assuming good bonding between resin and fiber.

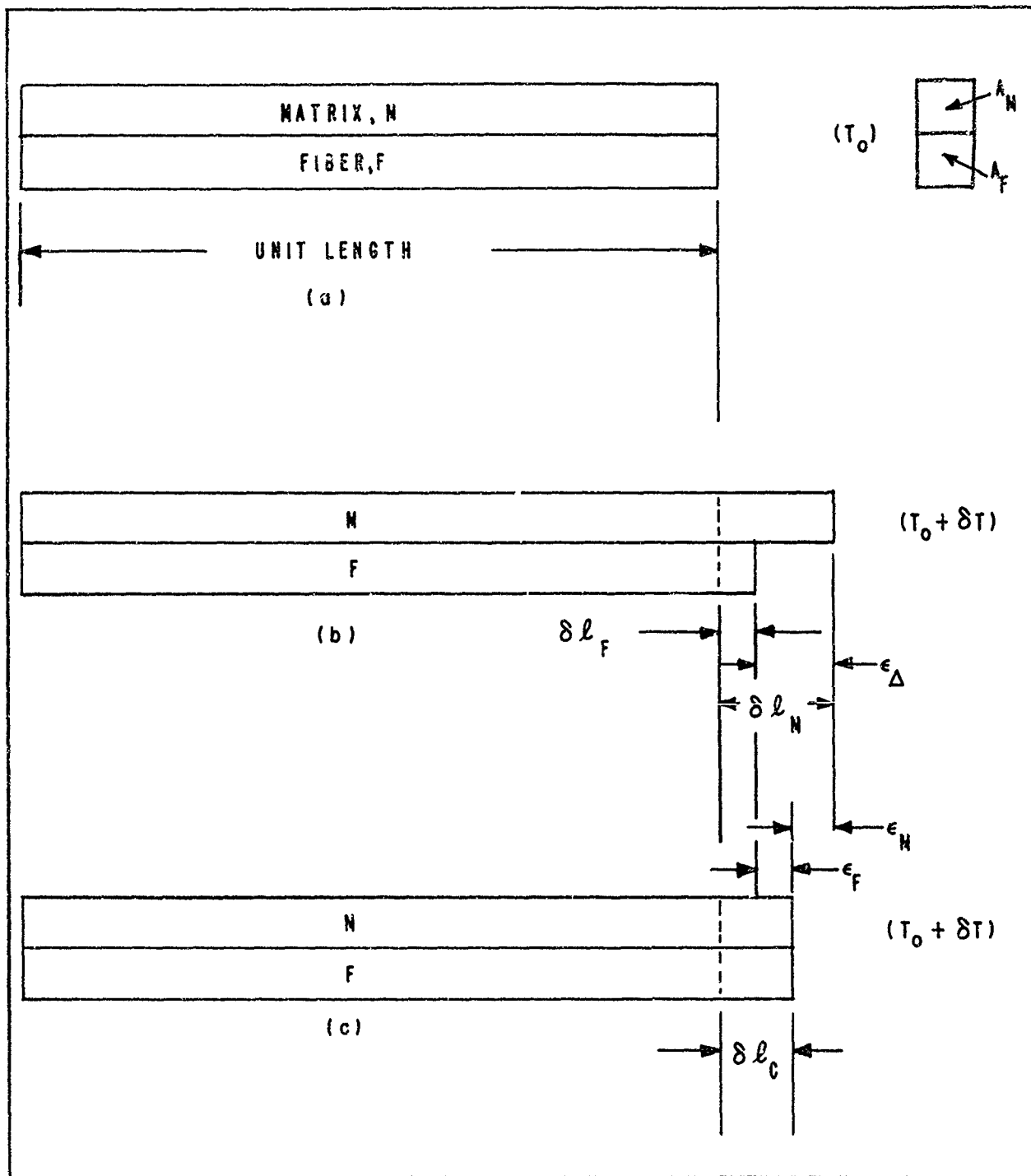


Figure 18. Schematic of Composite

As indicated in Figure 18:

$$\epsilon_M + \epsilon_F = \delta l_M - \delta l_F = (\alpha_M - \alpha_F) \delta T \quad (1)$$

where

α_M = coefficient of expansion of matrix

α_F = coefficient of expansion of fiber

Assuming purely elastic strain,

$$\epsilon = \frac{\sigma}{E} \quad (2)$$

where

σ = stress, psi

E = modulus of elasticity, psi

for stress equilibrium

$$\sigma_M A_M = \sigma_F A_F \quad (3)$$

from Equations 1 and 3

$$\sigma_F = \frac{(\alpha_M - \alpha_F) \delta T}{\frac{1}{E_F} + \frac{1}{E_M} \left(\frac{A_F}{A_M} \right)} \quad (4)$$

from Figure 18

$$\delta l_C = \delta l_F + \frac{\sigma_F}{E_F}$$

then

$$\alpha_C = \alpha_F + \frac{(\alpha_M - \alpha_F)}{1 + \left(\frac{E_F}{E_M} \right) \left(\frac{A_F}{A_M} \right)} \quad (5)$$

α_C = coefficient of expansion of composite.

For square weave fabric type reinforcement only half of the fibers are active in one direction, therefore:

$$\frac{A_F}{A_M} = \frac{\frac{1}{2} v_F}{v_M}$$

where

v_F = volume percent of reinforcement

v_M = volume percent of matrix

then

$$\alpha_C = \alpha_F + \frac{(\alpha_M - \alpha_F)}{1 + \left(\frac{E_F}{E_M}\right)\left(\frac{v_F}{2v_M}\right)} \quad (6)$$

The implicit assumption that the fibers are straight and parallel obviously does not hold exactly in fabric type reinforcements. However, since the lateral displacement of fibers due to weaving is small in comparison to fiber length, the errors should be small. The assumption of pure tensile and compressive stress in the matrix and fibers is reasonable since the fibers are long and the shear stresses are maximum at fiber ends as discussed in Reference 12.

The condition of elastic deformation in the matrix as given by Equation 2 may be limiting for polymeric materials. This is especially true at elevated temperatures, as above the glass transition temperature of phenolic resins.

For the materials considered in this investigation the necessary condition of good bonding between matrix and fibers is satisfied as indicated by the high strength levels of the composites.

The above model should be modified for fabric type reinforcements since biaxial stress is involved. As a first approximation the strain in the matrix in both directions parallel to fibers should be reduced by a factor of $(1-\mu)$. The coefficient of expansion in either warp or fill direction then becomes:

$$\alpha_C = \alpha_F + \frac{(\alpha_M - \alpha_F)}{1 + \left(\frac{E_F}{E_M}\right)\left(\frac{v_F}{2v_M}\right)(1-\mu)} \quad (7)$$

In the absence of accurate values for Poisson's ratio the calculations were based on Equation 6.

The material properties used in the calculations are given in Table 2. The calculated values of coefficient of expansion at room temperature agreed very well with measured values; the comparison is shown in Figure 19. However, at elevated temperatures the comparison is not favorable. For the A-2 material at 200°F a value of 3.0×10^{-6} in./in./°F is obtained from Equation 6 but the measured value is about 5.4×10^{-6} in./in./°F. The calculated value is based on a temperature dependence of elastic modulus of the resin as given in Figure 16. This measured temperature dependence of elastic modulus is not considered to be correct for the resin in matrix form in the composite. The measured modulus on resin castings (Figure 16) at 300°F is essentially zero, which indicates that the composite should expand as an unrestrained system of resin and fibers. High temperature expansion results do not indicate a free system of this type.

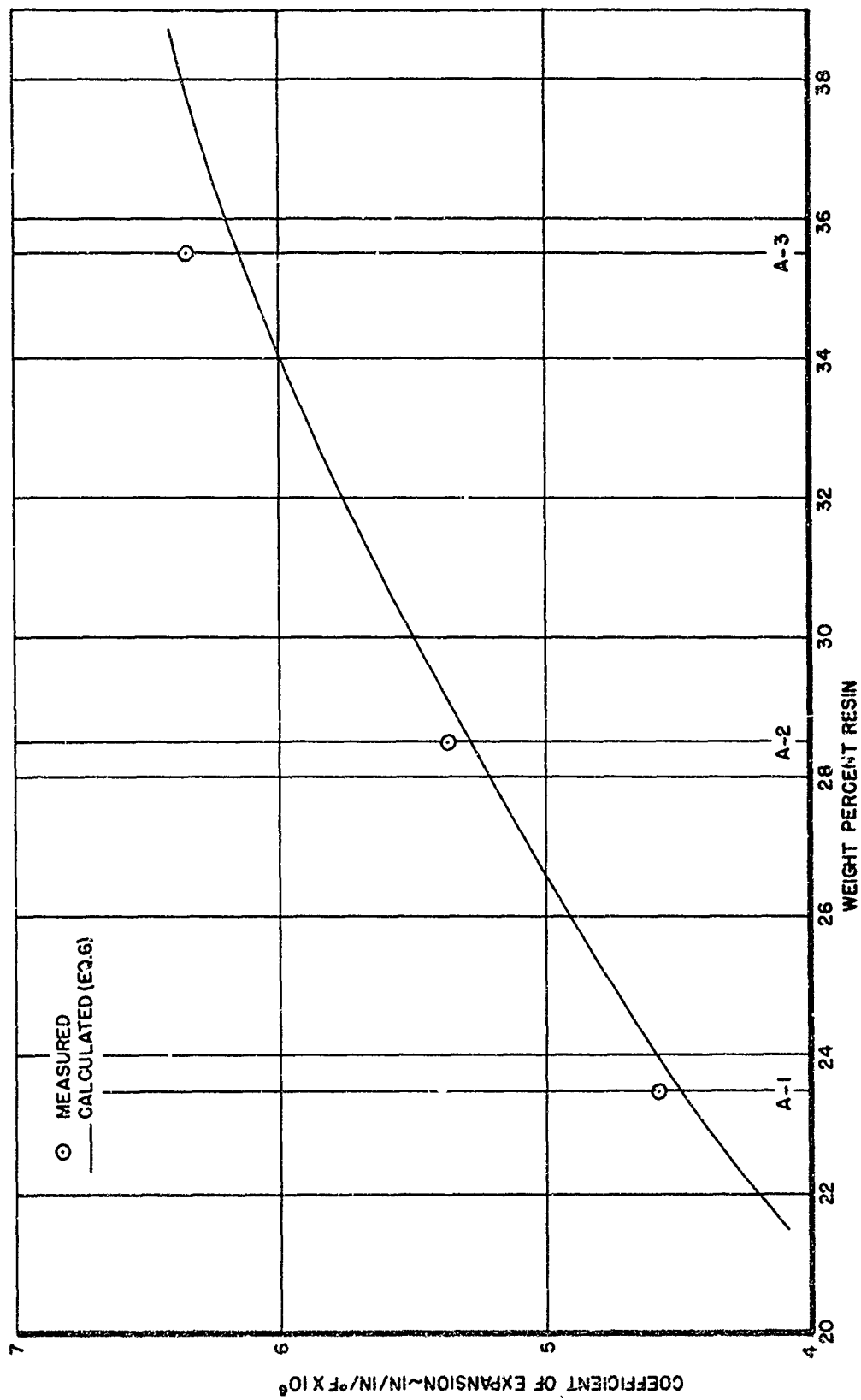


Figure 19. Room Temperature Coefficient of Expansion of Phenolic-Glass Fabric

TABLE 2
ROOM TEMPERATURE PROPERTIES OF MATRIX AND REINFORCEMENT

| Material | Temp °F | α_M in./in./°F (1) | α_F in./in./°F | E_M psi (2) | E_F psi (2) | v_F % | v_M % | E_F/E_M | $v_F/2v_M$ |
|-------------------|------------|---------------------------------|--------------------------|---------------------|---------------------|------------|------------|-----------|------------|
| A-1 | 75 | 46.0 | 2.5 | 0.49 | 11.0 | 62.5 | 33.1 | 22.4 | .925 |
| A-2 | 75 | 46.0 | 2.5 | 0.49 | 11.0 | 56.6 | 43.4 | 22.4 | .652 |
| A-3 | 75 | 46.0 | 2.5 | 0.49 | 11.0 | 49.4 | 50.6 | 22.4 | .488 |
| (1) See Figure 9 | | | | | | | | | |
| (2) See Figure 16 | | | | | | | | | |

It has been suggested (Reference 13) that matrix material in composites exhibit an effective modulus which can be considerably higher than bulk material modulus. This phenomenon is said to be a result of reduced lateral strain, that is, under axial tension or compression the thin film of matrix between fibers is restricted normal to fibers. The interfacial energy or bond strength, is considered to be the source of restraint. Under these conditions, Poisson's ratio is not applicable and the matrix strength and modulus are effectively increased. This phenomenon along with possible effects resulting from different fabrication conditions of the A-4 casting and the various laminates is considered to be a source of error in the high temperature modulus values.

CONCLUSIONS

Based on the discussion of the experimental results just given the following conclusions are drawn.

1. The dimensional stability of reinforced plastics, as reflected in thermal expansion properties, was shown to be extremely sensitive to thermal history and environmental conditioning. Samples of glass fabric reinforced phenolic composites conditioned in a dry environment at room temperature were found to have large non-linear variations in thermal expansion at elevated temperatures. This phenomenon was attributed to two effects, the first being loss of volatiles from the material as a result of further high temperature curing of the resin. The second contributing effect is the result of internal stress variation between the matrix and reinforcement. An inversion of these stresses at elevated temperatures results in erratic thermal expansion behavior. In general, these effects were less pronounced after repeated thermal cycling of a given sample, thus showing an "annealing" effect. Room temperature aging for prolonged periods also affected the expansion characteristics.

2. Thermal cycling produced no substantial change in the mechanical properties of the laminates studied and thus it was concluded that no gross changes in structural characteristics occurred.

3. Thermal expansion data on samples conditioned at several room temperature humidity levels yielded instantaneous coefficients of expansion which varied from about 5×10^{-6} to -5×10^{-6} in./in./°F. Since the magnitude as well as the sign of the coefficient change it is clear that an average value for the coefficient over large temperature ranges has little or no practical significance and should not be used for design calculations. The void content appears to be the most significant factor in controlling the magnitude of humidity or moisture effects. Void distribution would also be extremely important; however, this could not be correlated with the samples used in this program. To quantitatively assess this effect it would be necessary to fabricate samples with known and controlled void content and void distribution.

4. Analytical models for predicting the coefficient of expansion were employed in correlation of the experimental data. At room temperature the agreement was very good especially in terms of the dependence of expansion on the resin content of the composite system. The failure of the models to give the proper magnitude of the coefficient of expansion at higher temperatures is attributed to discrepancies in elastic modulus of the resin. It was concluded that the elastic constants measured on bulk resin castings were not the correct values for the thin film of resin

as found in composites. The quantitative validity of this conclusion would have to be substantiated by preparing samples with high resin content (60 to 80%), using single filament reinforcement. In this manner the resin would no longer be in thin film form and the properties of the resin should compare favorably with those measured on bulk resin casting.

5. To isolate effects of volatile loss and effects of internal stress variations it would be necessary to prepare samples with very accurately controlled cure conditions. A parametric study of cure temperature and time would yield information on the nature of the internal stress variations as reflected in thermal expansion anomalies. Detailed thermogravimetry would help resolve effects of resin cure and volatile losses.

APPENDIX A

MATERIALS

Material Fabrication

The materials used in this investigation were fabricated and machined by the H. I. Thompson Fiber Glass Company under Contract AF 33(657)-11164. Resin systems included a high-temperature MIL-R-9299 phenolic resin manufactured by Cincinnati Testing Laboratories, and marketed under the trade name of C.T.L. 91-LD. This resin was taken from a single lot supplied by American Reinforced Plastics, West Coast Distributors. Specific nomenclature and identification data is summarized in Table 3. The epoxy system was Shell Chemical's Epon 828, catalyzed with an aromatic amine mixture, B-3. This epoxy system is an intermediate cure system which facilitated the casting of the pure resin units. Latent cure-heat activated catalyst systems were not employed due to the high probability of excessive voids caused by the increased exothermic reaction rate at elevated temperatures.

The fiberglass cloth was of the commercial designation "112," a plain taffeta weave with a mean count of 40 warp yarns by 39 fill yarns. The 112 fiberglass employed with the 91-LD phenolic was finished with amine-type vinyl silane, commercially designated as A-1100 finish. The 112 fiberglass used in conjunction with the epoxy resin system was finished with methacrylate chromic chloride, commercially designated as Volan-A finish, in conformance with MIL-F-9084-A requirements. The method of impregnation utilized was the dip, flow, and metering method currently employed as state-of-the-art technology in commercial coating and impregnating facilities.

The "B" stage temperature is dependent upon the mass of the matrix material, resin content, and type of B stage desired. The glass reinforced phenolic materials were B staged at 200°F, varying time in heat to compensate for differences in resin content. The graphite reinforced phenolic material was staged at a slightly higher temperature of 220°F to compensate for the increase in mass and to maintain a similar staging cycle for the same resin content. The glass reinforced epoxy was staged at room temperature for 18 hours prior to laminating.

The predetermined number of plies were cut from each of the impregnated materials and stacked in an unnested position for laminating. Each of the thermal laminates was fitted with a thermocouple located at one-fourth the total laminate thickness, for a more precise monitoring of the laminate thermal history. Ultimate cure temperature cycles of three hours at 200°F, and one hour each at 250°, and 300°, and 350°F were used.

During the laminating cycle, laminating pressures were increased in 50 psi increment until a maximum pressure of 500 psi was obtained prior to laminate gelation. Laminates were cooled under maximum pressure until temperatures of 100° ±10°F were obtained.

The laminates were cut on an industrial diamond ~~as~~ prior to further processing. The physical test specimens were sanded on edge surfaces to produce a "true" edge. Thermal expansion specimens were cut to rough blocks (approximately 1/4 inch square) prior to machining to 0.240 inch O.D. cylinders. Machining was accomplished on a small engine lathe equipped with a tool post grinder and a diamond grinding wheel. The feed and cutting rates were adjusted to produce negligible frictional heating.

TABLE 3
DESCRIPTIVE NOMENCLATURE FOR COMPONENT MATERIALS

| Description & Lot No. | Source | Resins & Catalyst | | Type | Finish | Reinforcements | | General Name |
|--------------------------------------|---|-------------------|------------------------|------|---------|------------------|--------------|----------------|
| | | Trade Name | Generic Name | | | Weave | Trade Name | |
| Phenolic, High-Temp. C.T.L. 91-LD | American Reinforced Plastics L.A., Calif. | CTL 91-LD | Phenol - Formaldehyde | N/A | N/A | N/A | N/A | N/A |
| Epoxy Epon 828 | Shell Chem. Co. L.A., Calif. | Epon 828 | Bisphenol A Epoxy | N/A | N/A | N/A | N/A | N/A |
| Catalyst for Epon 828 | Shell Chem. Co. L.A., Calif. | B-3 | Aromatic Amine Mixture | N/A | N/A | N/A | N/A | N/A |
| Glass, Cloth | United Merchants | N/A | N/A | 112 | A-1100 | Plain of Taffeta | N/A | "E" Glass |
| Glass, Cloth | Clark-Schwebel | N/A | N/A | 112 | Volan-A | Plain or Taffeta | N/A | "E" Glass |
| Graphite, Cloth | National Carbon | N/A | N/A | WCB | None | Plain | WCB Graphite | Graphite Cloth |

The phenolic and epoxy resin systems were preformed prior to ultimate cure. The 91-LD phenolic resin was extremely sensitive to crazing and void formation during the cure cycle. This problem, related only to the 91-LD phenolic, was alleviated by first evacuating the resinous solution at room temperature and then subjecting the evacuated material to low temperatures of 140° to 150°F for extended times to produce the phenolic preforms. The degree of cure was approximated by the shore "D" hardness test, and the preforms were removed from the oven when a reading of 50 ±5 was obtained.

The ultimate cure for the epoxy resin billets was obtained by a standard oven cycle of three hours at 200°F, and one hour each at 250°, 300°, and 350°F.

Ultimate cure of the phenolic billets was a more complex problem, particularly in the areas of residual stresses and void formations that occur during ultimate cure. Curing and cooling under high pressures tend to minimize the internal stresses and void formations. Optimum clarity and laminate quality were obtained by compression-molding the 91-LD phenolic preforms. Crushed and ground phenolic powders were also successfully molded, but these parts have two basic limitations: (1) they are not optically clear, and (2) certain impurities are obtained in the grinding process, which are difficult to eliminate.

The phenolic resin billet utilized a cast resin preform fitted with an embedded thermocouple. The billet was molded at 1000 psi under the required standard cure cycle of three hours at 200°F and one hour each at 250°, 300°, and 350°F. The resin billet apparently did not reach ultimate cure under this cycle, as indicated by the zero barcol reading. A shore "D" hardness test was run and found to be 82 on this scale.

Physical Property Measurements

The specific gravity and density determinations were performed on randomly selected specimens from the thermal laminates and castings, in accordance with Federal Standard No. 406, Method 5011. The results are summarized in Table 1.

The ratio of resin to the total of resin and reinforcement is defined as the percent laminate resin content and is determined experimentally from randomly selected laminate specimens. To determine the resin content it is necessary to remove organic materials by ignition at 1000° ± 50°F until the weight of the remaining inorganic material is stabilized. The laminate resin content for the phenolic coated graphite materials was determined by calculating the theoretical raw cloth weight, and utilizing this as the final weight value in calculating the resin content. The raw cloth weight was determined experimentally by finding the average weight per square inch from large samples of the uncoated graphite cloth. This method is subject to material weight variation errors inherent in the base material, but is a realistic measurement when determined from large samples.

The degree of material hardness, or degree of polymerization, was determined for each of the materials with a calibrated Barber-Coleman Barcol Hardness Tester. A minimum of five determinations was taken on each of the prescribed materials, averaged, and the results tabulated in Table 1.

The specimens for void content determinations were selected from areas of the laminates in such a manner as to be adjacent to and representative of the thermal expansion specimens. The void content was determined from photomicrographs with the sampling technique described below.

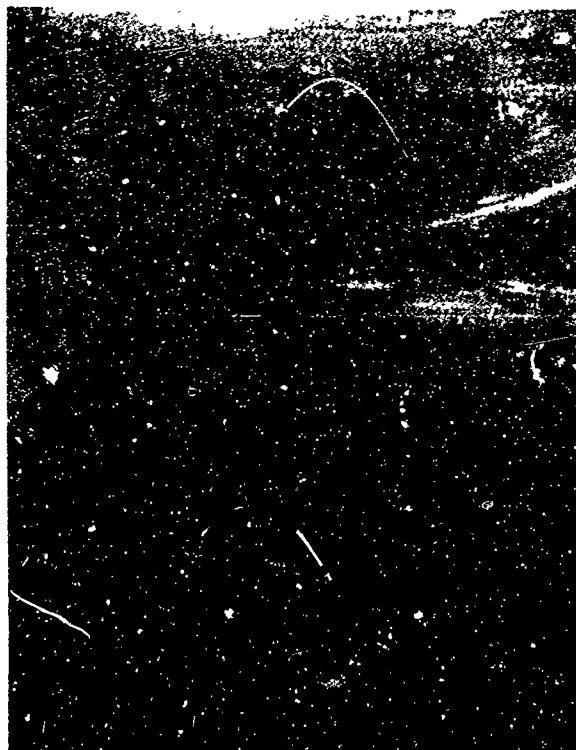
The area of a single observation is approximately 17 square millimeters under 350X magnification. It would be desirable to obtain an infinite number of observations, but this is not practical. Therefore, sampling plan was selected to yield five observations from each of two laminate surfaces for the composite laminates, and five observations from a single plane for the cast resin specimens. The sampling plan was developed by initially determining the x and y transversing range of the instrument. From these ranges a grid system was designed and assigned sequential numerical identification for all blocks. Observation blocks were selected from a random-number table, with the x and y coordinates located at the midpoint of the block. This block design was followed for all observations.

The photomicrograph determinations were performed on a Bausch and Lomb Metallograph, with the objective lens of 21.0 and oculars of 10.0 maintaining a Bellows distance of 30.5 centimeters for a total 350X magnification for the void content determinations. Polarized illumination proved to yield the optimum data for these determinations.

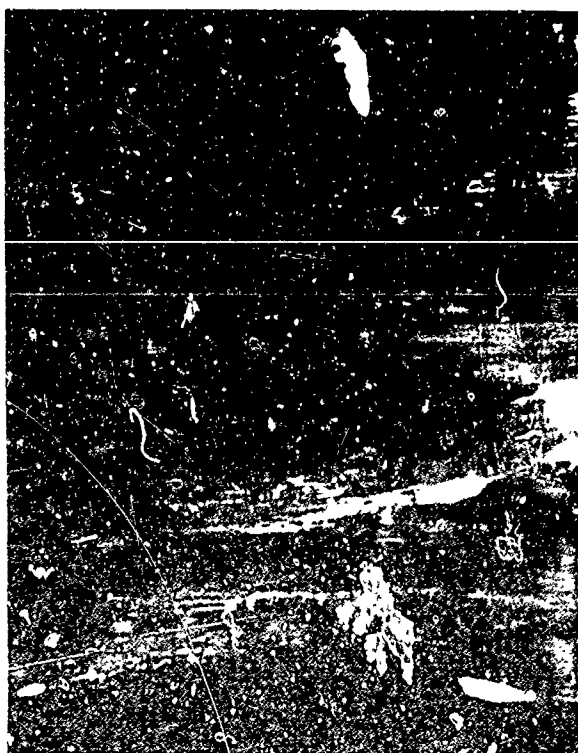
The microphotographs were enlarged to 1000X magnification, or four times their original size to facilitate void analysis. The number and size of voids were determined for each of the observations, then were tabulated and averaged to yield the void content. Representative photomicrographs of each material are shown in Figures 20 and 21. The results are summarized in Table 1.



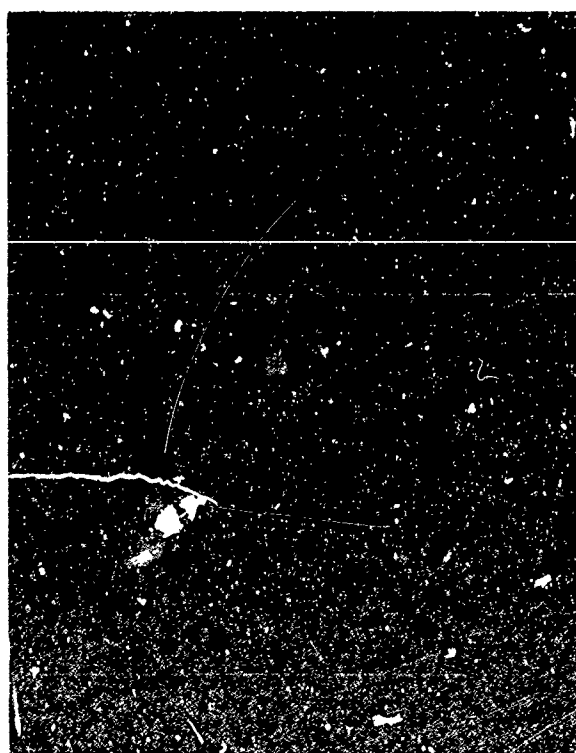
A - 1



A - 2



A - 3

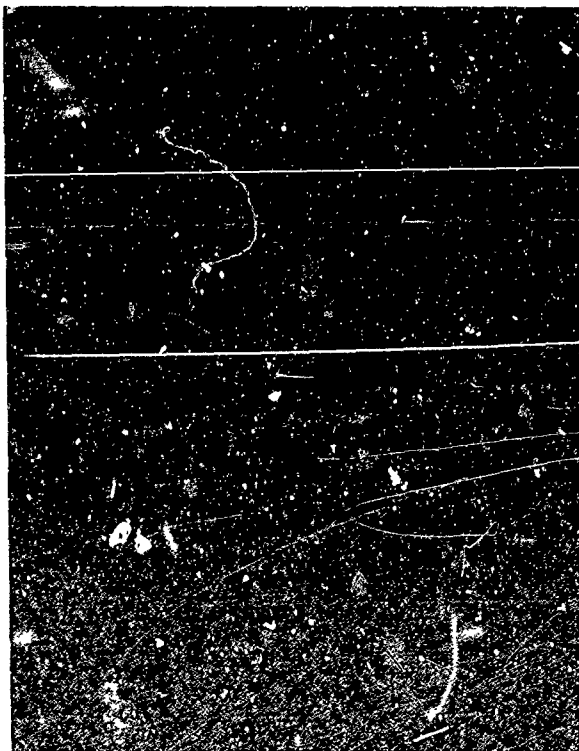


A - 4

Figure 20. Photomicrographs of Materials A-1, A-2, A-3, and A-4 (350X)



A-6



A-7



A-8

Figure 21. Photomicrographs of Materials A-6, A-7, and A-8 (350X)

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| <p>The effects of thermal cycling and variable thermal history on the dimensional behavior of reinforced plastic composites are presented. Thermal expansion was used as the primary independent variable in studying the wide variations in composite dimensions with thermal treatment, collectively termed thermal hysteresis phenomenon. The composites studied were those currently considered in structural and ablative applications.</p> <p>It has been found that the thermal expansion characteristics of a given composite may vary by more than 100 percent in cycling between room temperature and about 400°F. The most striking phenomena which is consistently observed is a decrease in the expansion coefficient to zero about 200°F followed by an increase at higher temperatures. Studies completed in analyzing this behavior included the following: (1) internal stress behavior of the composite as reflected in tensile and flexural modulus characteristics, (2) second order transitions of the polymeric matrix, (3) moisture absorption in the matrix, and (4) thermogravimetric analysis of the matrix and composite. Correlations between analytical model predictions and experimental performance were made on the various composites studied. Extensions of these models in explaining and estimating the dimensional behavior of other composite materials are discussed.</p> | |

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| <p>Thermal Expansion Reinforced Plastics Thermal Cycling</p> | | | | | | |

INSTRUCTIONS

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